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A special number in honour of
Leonard James Spencer, C.B.E., B.Sc., M.A., Sc.D., F.R.S.
Editor since 1900

THIS is to introduce the papers which have been sent in as a tribute to L. J. Spencer from Australia, Canada, England, France, Germany, Sweden, Switzerland, and the United States of America on the occasion of his completion of fifty years service as editor of the *Mineralogical Magazine*. To his many friends and colleagues the world over detailed comment on the quality of his work as an author, editor, and abstracter is unnecessary. He sets a standard difficult for us all to reach and has a critical faculty that extends beyond the confines of the two sciences he has followed so devotedly and light-heartedly, Mineralogy and Geology. Enthusiasm and perseverance are his 'signature tunes', both fortunately tempered by a sense of humour.

It has been an honour to remove a small burden from his shoulders on this occasion and the Council thanks those authors who, at short notice, have been able to send in papers.

F. A. BANNISTER

Frontispiece: L. J. Spencer, August, 1950

L. J. Spencer's work at the British Museum

By W. Campbell Smith

British Museum (Natural History)

LEONARD JAMES SPENCER, Keeper of Minerals in the British Museum (Natural History) from December 1927 to July 1935, joined the Department of Mineralogy officially on January 1, 1894, filling a vacancy caused by the death in 1892 of Thomas Davies. Davies had served in the Department since 1857. Trained by Nevil Story-Maskelyne, Keeper from 1857 to 1880, he had taken a great share in the arrangement and labelling of the mineral collection and in his later years had also had charge of the collection of rocks. Spencer was almost equally well qualified as a petrologist and as a mineralogist. He had studied chemistry at the Dublin Royal College of Science before going to Cambridge, where he studied geology as well as mineralogy and chemistry and gained the Harkness Scholarship for Geology in 1893. The examination for the vacancy at the Museum was held in August 1893 and Spencer was the successful candidate. Fortunately for mineralogy it was decided to assign him to work on the mineral collection, and at the request of the Keeper of Minerals, [Sir] Lazarus Fletcher, he went to Munich for three months (at his own expense) to study crystallography in Professor Paul Groth's laboratories. It was owing to this entirely voluntary period of study abroad that Spencer's appointment to the Museum staff was delayed until January 1, 1894, a delay which in later years operated to his disadvantage.

The staff of the Department when Spencer joined it consisted of [Sir] Lazarus Fletcher, Keeper since 1880, [Sir] Henry A. Miers, appointed 1882, and George Thurland Prior, appointed 1887. All three were Oxford men of high attainments.

The Department was well equipped with apparatus, and accommodation was adequate for the small staff of four scientific officers and five attendants. It consisted of four studies, chemical laboratory, balance room, librarian's room, clerk's room, and a lapidary's shop.

The work on the mineral collection when Spencer joined the Department was being done almost entirely by Miers. As described by Fletcher in successive annual returns, the scientific and executive work relating

to the collection included 'the preliminary examination of specimens submitted for purchase or exchange, the registration and incorporation of those recently acquired, the determination of the physical and geometrical characters, and the preparation of species-, variety-, and locality-labels'. All this work was in theory assigned to one assistant, but in fact the register of recently acquired specimens was kept by Prior in addition to his work in the chemical laboratory and on the rock collection.

Though the move of the collection from the British Museum building in Bloomsbury to the new museum at South Kensington had been completed in 1881, there was much work still to do on the arrangement of specimens in exhibition cases and in the cabinets. There was also in preparation a descriptive catalogue of all the specimens. This catalogue, usually referred to in the Department as the crystallographic catalogue, was a somewhat ambitious project started by the Keeper, Nevil Story-Maskelyne, in 1875 and described by him in his annual return for that year as a 'Scientific Catalogue of the whole collection, with crystallographic descriptions and chemical analyses of those specimens the composition of which it is desirable more accurately to determine'. This catalogue has not yet been completed nor has any part of it been published, but in the preparation of the materials for it successive assistants have found abundant subjects for original research, and the most important results of this work have been published in the *Mineralogical Magazine* from time to time.

Beyond the preparation of this catalogue there was no definite plan of research nor was the work of the assistants limited to any one branch of mineralogy, though Fletcher repeatedly stated in his annual returns that 'a mineralogist can no longer satisfactorily attempt both to keep abreast of scientific knowledge and to undertake original research in more than one of the three main branches (physical, petrological, and chemical)'.

For the brief period of two years Spencer was working with Miers on the mineral collection, and from him he had much information on its history and on the work that had already been done. With Miers's departure to take up the Professorship of Mineralogy at Oxford the whole of the work on the mineral collection was in Spencer's hands until G. F. Herbert Smith joined the Department in 1897. Herbert Smith on his arrival took over the work of selecting specimens offered for purchase or exchange, and the crystallographic catalogue for the halides and (later) oxides, and specialized in the study of physical (optical) characters

of minerals and gemstones, geometrical crystallography, and the improvement of optical instruments for this work.

There is no need to detail Spencer's work on the arrangement of the collections. It involved not only rearrangement in desk cases in the main gallery but, in addition, special exhibits of pseudomorphs, enclosures in crystals, artificial minerals (with Miers), models of famous diamonds (1901), and the setting up of large specimens in the pavilion (1895–97), and in case-ends. His rearrangement of calcites and aragonites led him to seek for rapid means of distinguishing aragonite from fibrous forms of calcite and he successfully achieved this, using specific gravity and optical characters, and published a paper on his methods in 1897.

He had to prepare for the printer the species-, variety-, and locality-labels, and he utilized a spare set of the locality-labels to make a topographical catalogue in book form of all the localities represented (1900). The Student's Index to the Collection of Minerals was also Spencer's care. He had assisted Miers with the new (20th) edition in 1895 and he himself prepared further editions in 1897, 1899, and 1903. He also assisted in the preparation of the 'History of the Collections', vol. 1, published in 1904.

Spencer's early publications were the direct outcome of his work on the crystallographic catalogue. He began by cataloguing pyrite which he finished in 1896, but he also had to bring up to date the catalogue for other sulphides, and by 1895 he was working on enargite and related minerals. His first paper written from the Museum in collaboration with G. T. Prior was on the aluminium phosphate, augelite, which up to 1894 was known only as a massive mineral. In June 1894 Spencer discovered crystals associated with bournonite and pyrite from Machacamarca, Bolivia. At first thought to be a new phosphate, the crystals were identified with augelite by comparison with specimens from the original locality, Westanå, Sweden, obtained from C. W. Blömstrand. The paper was read before the Mineralogical Society on November 20, 1894. A paper on enargite was presented to the Society in April 1895. This might have served as a model for the publication of the descriptive catalogue planned by Story-Maskelyne twenty years earlier. It gives: literature, complete list of forms starring those present on the Museum specimens, tables of angles establishing new forms, parameters, habits, twinning, parallel growths, identity with 'clarite', and a discussion of other minerals of similar composition, and, finally, a list of localities for enargite.

Other papers arising from Spencer's work on the crystallographic

catalogue followed in quick succession: 'Zinckenite and wolfsbergite (chalcostibite) from Wolfsberg in the Harz; and the zinckenite group'; and 'The crystallography of plagionite: new crystal forms on stephanite, enargite and anglesite'; and, with G. T. Prior, 'The identity of andorite, sundtite, and webnerite' (1897), and 'Stanniferous argyrodite from Bolivia: . . .' (1898), and three short papers on augelite, diaphorite, and miersite (1898). In 1899 he produced his paper on 'Plagionite, heteromorphite and semseyite as members of a natural group of minerals' with analyses by G. T. Prior, in which he discussed possible formulae for these minerals and, extending V. C. Butureanu's structural formula for plagionite to the other two minerals, indicated as most probable the formulae for pure crystals of the species which are those now adopted. In 1899 also the well-known paper by Prior and Spencer on 'The identity of binnite with tennantite; and the chemical composition of fahlerz' was published. The material for this investigation was partly derived from specimens collected by R. H. Solly from the famous quarry in the Binnenthal in 1898.

Another part of Spencer's work on the mineral collection involved the selection of specimens from collections presented to the Museum or offered for purchase. In 1894 he had arranged and labelled a small collection made by Lady Cust, and a much larger collection, 550 specimens, chiefly from Cornwall, formed by the Williams of Caerhays and presented by John Charles Williams in 1893. Specimens from Broken Hill, New South Wales, offered for purchase by J. R. Gregory in December 1897, and purchased in 1898, afforded the material for a paper on 'Marshite, miersite and iodyrite . . .' read to the Mineralogical Society in 1898 and published in 1901, and a later paper by Prior and Spencer on 'The cerargyrite group (holohedral-cubic silver haloids)' (1902). Spencer's descriptions in the earlier of these two papers of the behaviour of miersite and iodyrite when heated on a microscope slide are remarkably good as are also his conclusions on the mutual relations of these two minerals.

The work with Prior on andorite and sundtite, referred to above, and their work on augelite and argyrodite had already introduced Spencer to Bolivian sulphide minerals and fresh material was provided by the arrival of a collection made by Sir Martin Conway on an expedition to the Bolivian Andes in 1898. A paper on 'Crystallised stannite from Bolivia', read in November 1899, was the first of several contributions by Spencer on Bolivian minerals, largely encouraged in later years by his friend and school-fellow, T. Malcolm Roberts, who presented many

fine specimens from Bolivian localities. A full account of Sir Martin Conway's collection was published in an appendix by Spencer to Sir Martin's 'Bolivian Andes' in 1901.[1] In the matter of collecting he was not behindhand himself; indeed, as a boy he had formed a collection of minerals and fossils numbering some 3,000 specimens. In 1898 he had attended the meeting of the British Association at Bristol where he read two papers to section C (Geology) on 'Leadhillite in ancient lead slags from the Mendip Hills' and 'Supplementary list of British minerals'. He did some collecting in the Mendips that year, and the collection then made was referred to later in 1923 when he made a fresh visit to the district and discovered the new minerals chloroxiphite and diaboleite, collected some fifty good specimens of hydrocerussite, not previously recorded from the Mendips, and recorded and described also crednerite and wulfenite, new for that district.

In June 1902 as a result of [Sir] Lazarus Fletcher's persuasive powers a large number of fine specimens of gold ores from Australia were presented by the Government of Western Australia and several gold-mining companies. The material had partly been brought together for the Paris Exhibition of 1900, and had been shown at the Coolgardie Exhibition in 1899, Glasgow Exhibition 1901, and a Colonial Exhibition at the Royal Exchange in 1902. A paper entitled 'Mineralogical notes on Western Australian tellurides: the non-existence of "kalgoorlite" and "coolgardite" as mineral species', was published in February 1903. It included descriptions of altaite, calaverite, sylvanite, petzite, and coloradoite. The formula of coloradoite was proved to be HgTe, as for the original mineral from Colorado. Every fragment used in the analyses of the mineral was separately picked out and examined under a microscope before it was accepted.

A short 'Note on the pleochroism of adamite' from Chañarcillo, read in November 1903 (but not published until 1914) completes this account of the first ten years of Spencer's work on material in the Museum collections, but in addition he had accomplished much work at home on mineralogical literature. In December 1903 appeared 'A (third) list of new mineral names', the preceding lists having been published in 1897 and 1900. He had compiled the entries for, and edited, the mineralogy volumes (including petrology and crystallography) for the International Catalogue of Scientific Literature for 1901 and 1902; abstracted some 1,200 mineralogical papers for the Journal of the Chemical Society and,

[1] The paper on stannite (1901) contains a fine example of Spencer's crystal drawings with which he illustrated his papers.

finally, he and Mrs. Spencer had completed by December 1903 the translation of Max Bauer's 'Endelsteinkunde' (xvi+627 pages) which was published in 1904.

Spencer might well have felt satisfied with his first ten years' work at the Museum. Certainly his colleagues fully appreciated it, and the Geological Society showed its recognition of the value of his contributions to mineralogy by awarding him the Wollaston Fund in 1902.

The second decade of Spencer's work at the Museum takes us almost up to the beginning of the First World War. In 1904 important changes were made in the system of registering, labelling, and cataloguing the mineral collection. Some years previously G. T. Prior had started a slip catalogue of rock sections and it had proved its worth. Spencer now set about making a slip catalogue of the parts of the mineral collection for which he was responsible, beginning with copper. A slip was prepared for every specimen and on this was written all available information about it. It involved copying on to slips the register entries and all the details recorded for each specimen in the crystallographic catalogue. At the same time the numbering system was changed. From the beginning of 1905 every mineral specimen received two numbers; the year and a serial number. A fresh series of serial numbers began with every year. The adoption of the new numbering set free the serial numbers B.M. 87172 onwards for registration of specimens acquired before the General Register was opened in 1837 or belonging to large collections like the Allan-Greg collection acquired in 1860, which, having complete catalogues of their own, had never been entered individually in the departmental register. In the course of this cataloguing many specimens belonging to the historic collections of Sloane and Greville were identified. The minerals figured in James Sowerby's 'British Mineralogy' and 'Exotic Mineralogy' and in Miers's 'Mineralogy' were all identified and noted.

When the numbering system was changed the labelling system was also improved. Many of the old, coloured labels gummed on the specimens were perishing. With characteristic thoroughness Spencer attended evening classes in paper-making and paper-testing and used the knowledge so obtained to select the best kind of paper for the new labels. These were of two kinds: a small, gummed ticket for the number, to be affixed to the back of the specimen, and a so-called 'permanent' label, with printed heading, for permanently keeping with each specimen information as to the name of the species, associated minerals, the locality, and how and when it was acquired. All writing on the labels

was done in indian ink as it had always been in the registers and specimen labels previously. Similar care was exercised in the design of labels for microscope slides, and in the selection of card and paper for new specimen trays, and for locality labels for minerals and meteorites. A spare set of mineral locality labels had been used to form a topographical index of localities in 1900. This had been kept up to date, and the localities were also indexed alphabetically. In 1912, 683 new meteorite labels were printed and the opportunity was taken to print two sets on thin paper to form an alphabetical and topographical index of meteorites in the collection. Later (1914) spare sets of mineral locality labels were also printed on thin paper for use in the index.

In the Mineral Gallery most of the basic arrangement of cases was finished, but important collections were acquired and incorporated during this pre-war period; that of Miss Caroline Birley (3,000 specimens) in 1907, the Tendron bequest (1910), and a large selection of specimens from the Walker collection (219) in 1912. Guide labels drafted by Spencer giving case numbers of important species were affixed to pillars in the gallery in 1905, and new editions of the Student's Index were published in 1908 and 1914.

The year 1909 was marked by the appointment of the Keeper of Minerals, [Sir] Lazarus Fletcher, to be Director of the Natural History Museum, and G. T. Prior became Keeper in his stead. As an immediate result of Prior's promotion Spencer took over the general register from November 1909 in addition to his other work. He maintained this register in his own handwriting almost to the day of his retirement in 1935, only leaving to his trusted assistant, Miss J. M. Sweet, the registration of such large collections as that of C. O. Trechmann presented by Dr. C. T. Trechmann in 1926, the Liversidge collection bequeathed in 1927, and the Ashcroft collection of Swiss minerals, parts of which were presented in 1930, 1932, and 1935.

Spencer was responsible between November 1909 and July 1935 for over 20,000 entries in the current registers, all made with meticulous accuracy and consistency. The writing of labels from the register entries and the copying of the entries for the slip catalogue he entrusted to others, but if this work was in arrears he would take a hand at it himself. As a result of this great increase in Spencer's work on the register and the slip catalogue, some falling off in the volume of his original papers might have been expected. Nevertheless in the period 1904 to 1913 he produced thirteen papers under his own name as well as collaborations with other authors. His own papers included descriptions

of: irregularly developed crystals of zircon from Ceylon; phenakite from Tanganyika Territory; a 'Note on "feather-ore": identity of "domingite" (= "warrenite") with jamesonite'; further notes on some Bolivian minerals; and his well-known paper 'On hopeite and other zinc phosphates and associated minerals from the Broken Hill mines, North-Western Rhodesia' announcing the discovery of the two new species parahopeite and tarbuttite. With H. J. Johnston-Lavis he described a new mineral, chloromanganokalite, from Vesuvius, and he contributed notes on the crystallography of cassiterite pseudomorphs from Bolivia for Richard Pearce, and on bertrandite from Cornwall for [Sir] Arthur Russell. When examining crystals from Cornish tin furnaces sent in 1910 by his friend Richard Pearce, Spencer became convinced that crystals described as 'β-tin' by C. O. Trechmann in 1879 were identical with stannous sulphide. He completed his work on this material in 1910 but withheld publication until 1921 during the lives of authors principally concerned with the earlier papers. Other work in 1911 of which publication was postponed was on the crystallography and optical properties of the minerals celsian and paracelsian discovered in considerable quantities in old workings at the Benallt mine in Carnarvonshire by [Sir] Arthur Russell in 1911 and recorded in a letter to 'Nature' in that year.

In 1901 a special exhibit of a selection of models of famous diamonds had been arranged and Spencer had drafted descriptive labels for it. The discovery of the Cullinan diamond in 1905 aroused renewed and widespread public interest in the larger diamonds of South Africa. A glass model of the Cullinan was presented to the Museum by the Premier (Transvaal) Diamond Mining Company in 1906, and a temporary exhibit of models of famous diamonds was placed in the central hall from August 1907 to February 1910. As a result of his work on this exhibit Spencer wrote in 1910 'Notes on the weight of the "Cullinan" diamond, and on the value of the carat-weight', and in 1911 'The larger diamonds of South Africa'.

Between 1907 and 1910 Spencer made three visits on short vacations to the north of England to visit mines and mineral localities and to collect. The most important result of these collecting trips was his paper 'On the occurrence of alstonite and ullmannite (a species new to Britain) in a barytes-witherite vein at the New Brancepeth colliery near Durham', based on material obtained at the mine in 1909. The mine was revisited in 1946 on the field excursion of the Mineralogical Society, but no more ullmannite was found.

One cannot refrain from again mentioning the vast amount of bibliographical work Spencer did at home. Besides editing the *Mineralogical Magazine* and continuing his work on the International Catalogue of Scientific Literature, he also collaborated in the 'Tables annuelles de constantes et données numériques, de Chimie, de Physique et de Technologie'. He produced three more lists of new mineral names (1907, 1910, and 1913), 174 articles for the 11th edition of the 'Encyclopaedia Britannica', and 244 articles for Thorpe's 'Dictionary of Applied Chemistry'. In addition he translated the whole of R. Brauns' 'Das Mineralreich', v + 432 pages (1908–12), and wrote a very useful elementary treatise, 'The World's Minerals' (1911).

The War of 1914–18 brought little change in the routine work of the Museum. All the younger men were away on active service, but the work went on. Spencer added to his work outside the Museum the night duties of a special constable in his home district. A list of the more valuable specimens, compiled for the History of the Collections in 1903, was brought up to date. Many of these specimens were removed to a place of safety in 1918, but, except for the collection of gemstones, all were back in their places in the first week of January 1919. An improved topographical index for mineral localities represented in the collection was commenced in 1920.

Occasional accessions and purchases were fewer than usual in this period, but F. N. Ashcroft presented the whole of his collection of foreign zeolites to the Museum during the War (between 1914 and 1920), and Spencer registered them all as they came in and arranged a temporary exhibit of part of the collection in 1914. The collection of the Rev. John More Gordon was bequeathed to the Museum and incorporated in 1922. Spencer's published papers during the War were few: 'Crystals of iron phosphide (rhabdite) from a blast-furnace', and 'A butterfly-twin of gypsum' (1916). 'A (seventh) list of new mineral names', appeared punctually at its three-yearly interval in 1916. After the War he published on the mineralogical characters of turite (= turgite), new crystal forms of pyrites, calcite and epidote, fibrolite (= sillimanite) as a gemstone (1920), and on curvature in crystals (1921). The last was a collection of notes prepared for J. E. Stead, the metallographer, with whom Spencer collaborated in a paper on the ternary alloys of tin—antimony—arsenic in 1919. The paper on 'β-tin' and on the new lead-copper minerals from the Mendip Hills referred to above were published in 1921 and 1923, and his paper on 'Euclase and platinum from diamond-washings in British Guiana' was read in 1923. Up to this

time there had been no published record of the occurrence of platinum in British Guiana.

The eighth and ninth lists of new mineral names appeared in 1919 and 1922 and the first of Spencer's triennial 'Biographical notices of mineralogists recently deceased . . .' was published in 1921. He was still collaborating in the production of the 'Tables annuelles de constantes . . .' and editing the *Mineralogical Magazine*, but the outstanding achievement of Spencer's work in his 'spare' time in this period was the commencement of *Mineralogical Abstracts*. A scheme for the preparation of abstracts of mineralogical literature had been discussed by the Council of the Mineralogical Society in 1917, but the decision to publish *Mineralogical Abstracts* in their present form was taken at a meeting on January 20, 1920, and the first number of 16 pages was issued as an appendix to No. 88 of the *Mineralogical Magazine* in March of that year. It contained 38 abstracts, all by 'L.J.S.' It was intended that the Abstracts should cover the period 1915 onwards, so continuing the record of mineralogical literature compiled by Spencer for the Catalogue of Scientific Literature which had been brought to an end by the War in 1914.

In 1924 Spencer was invited to attend as a guest the Toronto meeting of the British Association, and a small grant made by the Museum enabled him to plan visits to the museums and mineral localities in Canada and in the U.S.A. Spencer set himself an extensive programme. He visited five localities in the province of Quebec, and eleven in Ontario including the silver-mines at Cobalt, and the gold-mines at Kirkland Lake, Porcupine, and Timmins in Northern Ontario, and three localities in Pennsylvania. He saw all the principal museums, four in Canada, eight in the U.S.A., the principal libraries in New York, Washington, and Boston, three research institutions including the Geophysical Laboratory at Washington, and some twelve private collections of minerals. At Rochester, N.Y., he went through Ward's stock of minerals with G. L. English, selecting 189 specimens for the Museum, and he selected for exchange specimens at the Royal Ontario Museum and at the Philadelphia Academy of Natural Sciences. In all he shipped back to the Museum about 12 cwt. of mineral specimens. The total cost to the Museum (exclusive of the purchase from Ward's) was £41. 5*s.* 9*d.* Among the minerals secured were twelve of species new to the collection.

The Jubilee meeting of the Mineralogical Society was held in London in 1926 and Spencer joined the field excursion to the north of England

led by Professor Arthur Hutchinson, visiting numerous mineral localities and mines in Cumberland, Westmorland, the Alston district, and Weardale.

His published papers about this time included the description of two new minerals; schultenite from South-West Africa, and aramayoite from Bolivia, both described in 1926. The schultenite was discovered on a specimen labelled lanarkite from Tsumeb; the aramayoite on a specimen from the Animas mine at Chocaya, Potosi, found and recognized as probably a new mineral by T. Malcolm Roberts.

Another new mineral, described in 1928, was potarite, PdHg, discovered in British Guiana by Sir John Harrison in 1924 and 1925. Spencer had previously identified as allopalladium three tiny grains of the same material. He had correctly and skilfully detected palladium, but the mercury had eluded him. The largest of the three grains he had to examine weighed 76 milligrams.

Other papers of this period were 'An inclusion of magnetite in diamond' (1924), and on arrow-head corundum twins from the Zoutpansberg district, Northern Transvaal (1927), and on the wonderful sperrylite crystals from Tweefontein farm, Potgietersrust, Transvaal, (1926). The two sperrylite crystals described measured $5{\cdot}5 \times 5{\cdot}3 \times 5{\cdot}0$ mm. and $18{\cdot}5 \times 16{\cdot}5 \times 15$ mm. along their cubic axes, the larger one weighing 33·75 grams. The sperrylite crystals from Vermilion mine, Sudbury, Ontario, described in 1889 measure about 0·5 mm. across.

Before he retired from the Museum Spencer had a hand in the description of yet one more new mineral, bismutotantalite from Uganda, described by E. J. Wayland and Spencer in 1929. He also contributed a note on the crystallography of zunyite from Postmasburg in a paper by L. T. Nel in 1930. The paper on 'Fictitious occurrences of iron silicide (ferrosilicon)', published in 1935, was the result of work done in 1924 and 1929. The last purely mineralogical paper published before he retired was his description of the splendid, colourless crystal of euclase, obtained from H. R. Ruggles-Brice, by whom it was found on the Lukangasi mica mine, Morogoro district, Tanganyika Territory, and of phenakite crystals from Klein Spitzkopje, in South-West Africa.

The last ten years of Spencer's service at the Museum brought him honours and promotion which were richly deserved. He was elected a Fellow of the Royal Society in 1925, appointed to a Deputy Keepership in the Museum in June 1927, and he succeeded G. T. Prior as Keeper of Minerals in December of the same year. He was appointed a Commander of the Order of the British Empire in 1934. He was awarded the

Murchison Medal of the Geological Society of London in 1937, two years after his retirement from the Museum.

There were several changes in the staff of the Mineral Department during this period. E. D. Mountain, who had filled the vacancy caused by Herbert Smith's appointment as Assistant Secretary (later Secretary) of the Museum in January 1921, resigned in December 1926 to take up a lecturership in Geology at Rhodes University College, Grahamstown, South Africa. F. A. Bannister was appointed to the Department in September 1927, and Miss J. M. Sweet had joined the staff in June of the same year. Max H. Hey was appointed in November 1928, and took over Prior's work as chemist, the cataloguing of the zeolites, and, later, of the meteorite collection.

With this staff of assistants to help him, Spencer was able to devote time and energy to developing his plans for improved exhibits in the gallery and to contacts outside the Museum. Cases at the entrance to the gallery previously used as book-cases for periodicals were provided with internal lighting and filled with attractive exhibits. The upper panes were used for large transparencies (added in 1930), and one case was arranged (in 1928) very skilfully to show the beautiful effects of fluorescence of minerals in ultra-violet light. Already in 1927, in his paper on 'South African occurrences of willemite', Spencer had added a note on the 'Fluorescence of willemite and some other zinc minerals in ultra-violet rays', using for his experiments a mercury-vapour lamp. He had seen high-tension sparks used at Franklin Furnace for the detection of willemite in ore and on the washing-tables, and as he recalled in a later paper, he had attended in 1892 a short course of lectures on fluorescence by Sir George Stokes, and the experiments performed in a beam of sunlight admitted through a slit in a window shutter had remained a vivid recollection. The new fluorescence exhibit was described in a paper in 'The Natural History Magazine' in 1928. It was probably the first public exhibit of its kind. It attracted great interest, and similar exhibits have since been set up in many natural history museums and private collections, particularly in the U.S.A.

In 1929 Spencer left on the second of his long journeys abroad. He attended the British Association meeting in Cape Town and Johannesburg, and the International Geological Congress in Pretoria, at which he was one of the British Government delegates. On this trip he covered 7,500 miles by rail and 1,500 by car, visiting amongst other places the Kimberley diamond mines and the Vaal River diggings, the gold-mines of the Rand, the Premier Diamond mine, the Bushveld and Pilansberg

in South Africa; Livingstone, Lusaka, Bwana M'Kubwa, and N'Kana; and he collected much material at Broken Hill, Rhodesia. In South-West Africa he visited the diamond-fields at Luderitz Bay, copper mines at Tsumeb, the vanadium mine at Grootfontein, Windhoek, and several localities in the Namib desert. At Windhoek he saw in the Public Garden a pile of some thirty masses of meteoritic iron from Gibeon, and near Grootfontein he examined the largest known meteorite, an iron estimated to weigh 60 metric tons, which lies where it fell on Hoba West farm. Altogether 17 cases of minerals were shipped home after this South African trip, and he secured the promise of many other specimens, including a 136 kilogram mass of the Gibeon iron, presented to the Museum by the Administration of South-West Africa.

During Spencer's absence in Africa the redecoration of the Mineral Gallery had been completed, and on his return a start was made on the provision of new wall-cases. These cases fitted with glass shelves and internal lighting enabled the best of the large mineral specimens to be seen to advantage for the first time. [A description of the lighting arrangements in the new cases and in the older cases outside the gallery was given in a paper in the 'Museums Journal' in 1932.] The first of these new cases was completed in time for the fiftieth anniversary of the opening of the Natural History Museum in 1931. The celebration was postponed from April 18 to September 29 so that it should coincide with the meeting of the British Association in London, when many delegates from home and overseas visited the Museum.[1]

Spencer always kept in mind the needs of visitors, and in 1930 he produced a 4-page guide leaflet to the Mineral Gallery for free distribution. 10,000 copies were printed for each edition, and by 1934 it had run through five editions. Later work in the Mineral Gallery to which Spencer devoted his attention was the exhibit of the gemstones of the Sir Arthur Church collection and of the Clarke-Thornhill collection, the latter bequeathed to the Museum in 1934. He published an account of these collections in 'The Gemmologist' in 1934 and later in the same year papers on 'Pollucite, a new gemstone', and 'Sir Hans Sloane's precious stone collection'. Earlier he had described in 'The Natural History Magazine' a magnificent crystal of aquamarine from Minas Geraes, weighing 2,505 grams and measuring 13 cm. in height, and a crystal of topaz from Madagascar, weighing 2,290 grams (1927 and 1928).

[1] At this meeting of the British Association, Spencer gave 'A Second supplementary list of British minerals', bringing up to date the list given at the British Association meeting in Bristol thirty-three years earlier.

A paper on 'Gemstones in the Museum collection . . .' was published in the first volume of 'The Gemmologist' in 1931, and a short paper on Pebbles, in very popular style, was contributed to the same journal in 1934. The latter paper resulted from the acquisition in 1934 of a large collection of pebbles presented by E. J. Dunn of Melbourne, Australia.

Spencer's visits to Windhoek and Grootfontein had renewed his interest in meteorites, and on his return he had published a paper on 'Meteoric irons from South-West Africa' describing the Gibeon iron, and Hoba, and he gave a more detailed account of the Hoba meteorite (with chemical analysis by M. H. Hey) in 1932. Six other individual meteorites were described between 1930 and 1935, and in addition many papers were published on meteorite craters and tektites referred to below. A very useful paper on 'Pseudometeorites' was published in 'The Natural History Magazine' in 1931. Meteorites were soon to claim much of Spencer's attention. The discovery of the new meteorite craters at Henbury (1931) and Wabar (1932) fired his enthusiasm more than anything else had done. He described the meteoritic iron and silica-glass from the Henbury craters and from Wabar in a paper published in 1933. The great collection of the meteoritic irons from Henbury acquired in 1932 by presentation, purchase and exchange; the silica-glass from the meteorite craters at Wabar discovered by H. St. J. B. Philby, and the still unexplained masses of silica-glass found in the Libyan Desert by P. A. Clayton in 1932, were all subjects of special exhibits arranged by Spencer, as also an exhibit of the collection of stones from the shower of meteorites from Tenham (Queensland) acquired in 1935. His discovery of the presence in the black parts of the Wabar glass of minute spheres of nickel-iron representing a 'rain' or rather 'drizzle' of molten metal, condensed from iron and nickel vapours, was astounding but convincing evidence of the very high temperatures and the local exhaustion of atmospheric oxygen during the explosion caused by the impact of large crater-forming meteorites. He published papers on meteorite craters in 'Nature' and in 'The Geographical Journal' in 1932 and 1933, as well as some notes on the origin of tektites in 'Nature' and in the 'Comptes Rendus' (Paris). Then came the discovery by P. A. Clayton of the remarkable silica-glass in the Libyan Desert. Its origin was a complete mystery. There was every hope that meteorite craters would be found in the vicinity of the glass, and although now in his sixty-fifth year Spencer eagerly accepted an invitation to join an expedition in December 1934, organized by the Survey of Egypt, with O. H. Little and

P. A. Clayton, inspector of the Egyptian Desert Surveys. The expedition found no trace of meteorite craters among the high sand-dunes surrounding the locality and the origin of the Libyan Desert glass remains unsolved, but great quantities of the glass were obtained and a full survey of the locality was completed.

After his return from the Libyan Desert Spencer made yet one more short collecting trip before he retired. This was an attempt to secure the entire contents of a small stalactite cave in the Carboniferous Limestone with a view to setting it up again in the Museum, a project Spencer had had in mind ever since his very early days in the Department. A small cave was broken into in a quarry near Shepton Mallet, Somerset, in April 1935. Spencer went down at once to make arrangements. Unfortunately the cave had to be cleared quickly to make way for further quarrying and time did not allow of elaborate plans. With two quarrymen to assist him Spencer brought away 10 cwt. of fine stalactites and stalagmites, and a small group of these was eventually (1939) set up in a case outside the Mineral Gallery.

In May and June 1935 a little time was spent in clearing up odds and ends before the day came for Spencer to retire on July 8, but the secret of Spencer's great output of work was that a task undertaken was carried through, and he left very little work unfinished. His note-books, bound in twenty-eight neatly indexed volumes, are available in the Mineral Department library for future reference.

Of those who were at the Museum when Spencer arrived in 1894 all had long since retired, but two of the Experimental Officers have served with him since 1906. They, and the younger men, remain to carry on the methods Spencer taught for the care of the mineral collections and the library. To them and to those who preceded them the Department owes much, and Spencer would be the first to acknowledge the value of their work.

Happily Spencer's retirement from his official position in the Museum has not severed his connexion with the Department of Mineralogy. Devoting his time almost entirely to the preparation of *Mineralogical Abstracts* and to editing the *Mineralogical Magazine*, he is a constant visitor to the departmental library. Always interested in the work of the Department, he is ever ready to assist with advice and with information from his vast store of knowledge those who are trying to carry on the high standard set them during his forty years' service in the British Museum.

Clay derived from sillimanite by hydrothermal alteration

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THE association of clay minerals with sillimanite near Williamstown, approximately 23 miles north-east of Adelaide, South Australia, has been noted by the writer in earlier papers (Alderman, 1942, 1950). These papers described the occurrence of quartz-sillimanite and quartz-kyanite rocks and gave the evidences which suggest that they were formed metasomatically by alumina-rich fluids at high temperatures. It was also suggested that as the alumina-concentration and temperature of the fluids decreased the metasomatic activity was followed by a period of pegmatite formation which, in turn, gave way to a hydrothermal stage. Brief reference was made to the conversion of sillimanite to clay by hydrothermal agencies.

The clay is well exposed and has been mined for many years as it has excellent refractory qualities. Irregularly distributed throughout the comparatively soft clay material are discrete masses of extremely hard sillimanite-quartz-rutile rock. These are of very variable size and may measure up to several feet in diameter. In the course of mining operations the clay is separated from the sillimanite masses which are also a source of refractory materials.

The textural similarity of freshly broken surfaces of the clay and sillimanite rock as well as their relationship in the deposit strongly suggest that the clay has been formed by alteration of the sillimanite. This contention is thoroughly confirmed by more precise methods of examination, as will be described later in this paper.

Conversion of sillimanite to clay seems to have taken place along certain definite 'pipes' or channels. Even in such channels the alteration was not by any means complete, as the large masses of quartz-sillimanite rock are almost certainly residuals which have escaped conversion. Also, as described in more detail later, the clay itself always contains a considerable amount of fine unaltered sillimanite. Away from

the areas of alteration quartz-sillimanite rock occurs in massive form and is not associated with clay.

Sillimanite rocks.

In hand-specimens the sillimanite rocks are generally white, flecked with red rutile, and their uniformly fibrous texture gives them a most unusual degree of toughness. In general they can be referred to as quartz-sillimanite-rutile rocks in which the relative amounts of the three components vary widely. In some specimens the volume-percentage of sillimanite may be as high as 98 %, in others quartz is the most plentiful component. Rutile contents up to 3 % are quite usual. Varying but generally small amounts of clay mineral are present in the sillimanite masses which are obtained from the clay mines. Occasional grains of kyanite and its alteration product, damourite, frequently occur in association with quartz veinlets. The more quartzose varieties often show a rough banding in which quartz-rich bands alternate with bands richer in sillimanite.

A typical analysis of quartz-sillimanite-rutile rock is ('Mining Review', 1940): SiO_2 41·26; TiO_2 2·70; Al_2O_3 54·35; Fe_2O_3 0·59; FeO n.d.; MgO 0·08; CaO 0·44; Na_2O 0·02; K_2O nil; H_2O+ 0·40; H_2O- 0·02; CO_2 nil; total 99·86.

The analysis suggests that this sample contained approximately 86 % sillimanite, 9 % quartz, and 2·7 % rutile. One of these rocks which consists almost entirely of finely fibrous sillimanite is illustrated in fig. 1.

Clay rocks.

The outstanding feature of the clay rocks is the invariable presence of a considerable proportion of sillimanite. This occurs as fine needles and groups of fibres which have escaped hydrothermal alteration to clay. The fibres vary in length from several millimetres down to two or three microns. The size of the smallest fibres makes both the complete separation of sillimanite from clay and a satisfactory determination of the relative amounts of these two components matters of great practical difficulty.

The clay component proves to be kaolinite, although there are certain indications that a small proportion of dickite may also be present. Rutile has a distribution similar to that in the original sillimanite rock. The proportion of quartz is variable, as it is in the sillimanite rocks, and the matter remains uncertain as to whether it has increased or decreased as a result of the hydrothermal activity. A small amount of diaspore is

present in some samples and is presumably a by-product in the conversion of sillimanite to clay. Also present are irregularly distributed

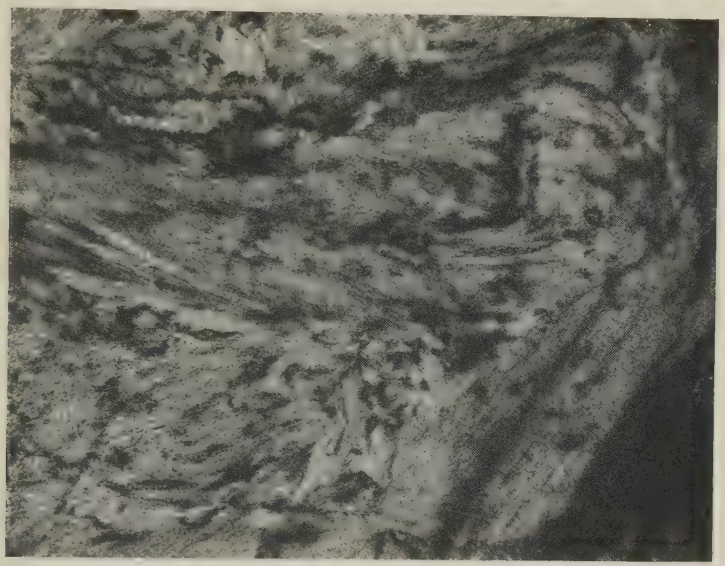

FIG. 1. Thin section of unaltered sillimanite rock. The whole of the field is occupied by uniformly fibrous sillimanite. Parallel nicols, ×52.

amounts of damourite derived from the alteration of kyanite, relics of which can also be recognized in some samples.

Typical analyses of clay rocks are (Jack, 1926):

	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	FeO	MgO	CaO	Na_2O
1 ...	44·04	0·52	44·74	0·29	n.d.	nil.	0·32	0·39
2 ...	42·86	0·04	47·96	0·30	n.d.	0·12	0·04	0·18

	K_2O	H_2O+	H_2O-	CO_2	Cl	Total
1 ...	0·19	9·10	1·00	nil.	0·04	100·63
2 ...	0·41	8·00	0·60	nil.	0·01	100·52

Considering only the four main mineral components these analyses suggest that the approximate compositions of these samples were (1) kaolinite 65 %, sillimanite 30 %, quartz 3 %, rutile 0·5 %; (2) kaolinite 57 %, sillimanite 40 %, quartz 1 %, rutile trace. Despite the limitations of such calculations these figures seem to give a reasonable estimate of the actual proportions of minerals present in samples typical of the material mined for refractory clay.

Microscopic examination of thin sections of the clay rocks gives a very clear picture of the alteration of sillimanite to clay. The hydrothermal

fluids seem to have worked their way between the sillimanite fibres as well as across the fibres following lines of transverse fracture. This dismembering of the sillimanite aggregates is accompanied by a lowering of birefringence and eventually by complete breakdown into finely granular aggregates of clay. The reproduced photograph (fig. 2) illustrates these features.

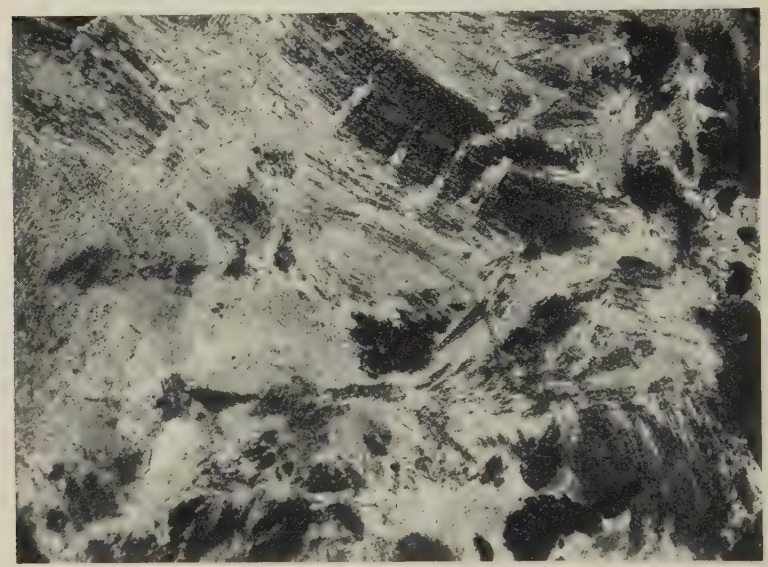

Fig. 2. Thin section of clay rock. Dark areas are mainly sillimanite, light areas mainly kaolinite. The large sillimanite aggregates show alteration to kaolinite parallel to the fibres and along lines of transverse fracture. Ordinary light, $\times 52$.

Narrow shear-zones in the clay rocks are filled with remarkably pure kaolinite. The movement in these shears must have been small although the surfaces of the clay show well-developed slickensides. It is uncertain whether the movement caused mechanical segregation of kaolinite into narrow veins or whether the kaolinite was deposited from solution into earlier-formed fissures. Small areas in these veins consist of kaolinite alone, although most specimens also contain small amounts of sillimanite and quartz which, however, are in much smaller proportion than in the massive clay rocks.

Clay mineralogy.

In thin section the clay mineral is colourless and, as is usual, too fine-grained to allow satisfactory determination by optical methods.

Some flakes which were larger than the average appeared to show a positive optical character which suggested that the mineral was dickite rather than kaolinite. However, staining methods, X-ray examination, dehydration curves, and electron microscopy all indicate that the bulk

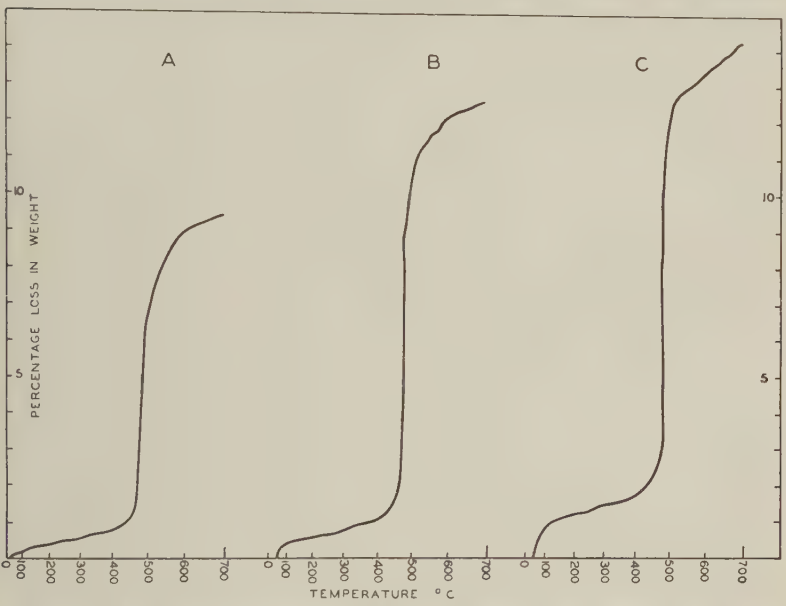

Fig. 3. Dehydration curves of:—*A*. Fine fraction from massive clay rocks, Williamstown. *B*. Kaolinite from shear-zone, Williamstown. *C*. Kaolinite, Cromer ('Cromer C' clay).

of the clay mineral is kaolinite while allowing the possibility, or giving some indication, that a small proportion of dickite is also present. Some of the larger and more flaky fragments do not, for instance, become stained by methylene blue to the same extent as the bulk of the finer clay. X-ray powder photographs, as made and commented on by Dr. A. L. G. Rees, indicate that the clay is largely kaolinite, although the relative intensity of the 1·79 Å. reflection suggests the presence of some dickite.

The dehydration curves (fig. 3) were made by Mr. A. J. Gaskin using a controlled, self-recording dehydration apparatus which he has developed. Of the three curves shown in the diagram curve *A* represents the fine fraction of the massive Williamstown material. The low total-water loss shown by this curve indicates that the sample contained a considerable proportion of non-hydrated mineral, which in this fraction

would be almost entirely sillimanite. The proportion of water lost in the range 500–600° C. is appreciably greater than would be expected from a 'pure' kaolinite. This favours the suggested presence of some dickite which loses most of its water at about 540° C. (Ross and Kerr, 1930). However, the main water loss of this sample takes place at a little less than 500° C. which is normal for kaolinite.

Curve *B* represents clay from the same deposit but from the shear zones which have been referred to above. The proportion of non-hydrated impurity in this sample is much lower than that from the massive clay represented by curve *A*. The curve indicates a fairly pure kaolinite.

Curve *C* is included for purposes of comparison. It represents a reasonably pure kaolinite from Cromer, a deposit in the same district but of entirely different origin. The Cromer clay was derived from hydrothermal alteration of pegmatitic felspar and has no connexion with the sillimanite rocks of Williamstown.

The electron micrograph (fig. 4) illustrates a fine fraction of the normal Williamstown clay. Kaolinite, showing typical outlines, constitutes the bulk of the material. The long narrow aggregate is assumed to be a fibre of sillimanite, which is known to be present even in these fine-grained fractions, and gives striking evidence of the difficulties of making a clean separation of the clay minerals.

Discussion.

The point of greatest interest in the Williamstown kaolinite is its derivation from sillimanite. As far as the writer is aware no similar occurrence has previously been described, although Dr. H. von Eckermann has mentioned (Alderman, 1948, discussion) that in the migmatites around the Alnö alkaline intrusion sillimanite is altered to montmorillonite.

It has been suggested in more detail elsewhere (Alderman, 1942, 1948) that the quartz-kyanite and quartz-sillimanite rocks owed their origin to metasomatic agencies in which alumina-containing fluids of high concentration and at elevated temperature reacted with various members of a series of pre-Cambrian schists. As the temperature and alumina-concentration became lower a pegmatite phase ensued in which quartz-kyanite-oligoclase-pegmatites were formed and were followed later by normal quartz-orthoclase-mica-pegmatites. By the end of the pegmatitic phase the active fluids apparently consisted largely of water with silica and some potassium. The reactions produced by these

fluids can best be described as hydrothermal. The earlier-formed kyanite and sillimanite were unstable under these hydrothermal conditions, kyanite being altered to damourite and sillimanite to clay.

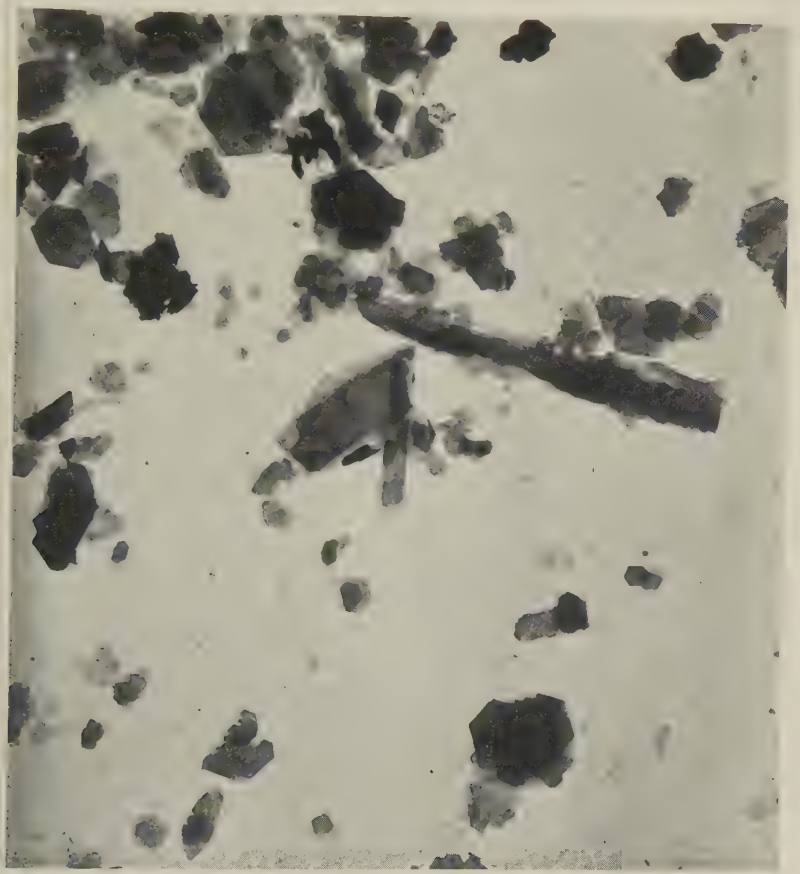

FIG. 4. Electron micrograph of fine fraction of Williamstown clay. Most grains show typical kaolinite outlines. The long aggregate is assumed to be a fibre of sillimanite. ×15,000.

The reactions involved in the kaolinization of sillimanite appear to be simple and in a general way can be represented by the equation:

$$(1)\quad \underset{\text{sillimanite}}{2Al_2SiO_5} + 4H_2O + 2SiO_2 \rightarrow \underset{\text{kaolinite}}{Al_4Si_4O_{10}(OH)_8}.$$

This equation assumes that there was sufficient silica in the hydrothermal fluids, or made available from quartz in the adjacent rock, to

convert sillimanite completely to kaolinite. This, however, could not have been entirely so, as a small amount of diaspore is distributed throughout the clay rocks. It is suggested therefore that to some extent the reaction may have followed that given in equation:

$$(2)\quad \underset{\text{sillimanite}}{4Al_2SiO_5} + 6H_2O \rightarrow \underset{\text{kaolinite}}{Al_4Si_4O_{10}(OH)_8} + \underset{\text{diaspore}}{4AlO(OH)}.$$

The reaction given in equation (1) was probably much the greater factor in the process of kaolinization. The extent to which the silica involved in this reaction was derived from quartz in the sillimanite rocks is uncertain. The quartz-sillimanite ratio in these rocks is almost infinitely variable and it is generally impossible to judge the original quartz-content of any of the present clay rocks. However, some unaltered sillimanite rocks contain very little quartz, and representatives of this sillimanite-rich type have apparently become kaolinized. As the diaspore content of these rocks is very small, it would appear that the hydrothermal fluids must have contained very nearly enough silica to effect the reaction suggested by equation (1) without the help of silica from adjacent quartz.

The conversion of kyanite to damourite seems to have been analogous to the kaolinization of the sillimanite but involves the presence of potassium. The hydrothermal fluids thus apparently consisted very largely of water and silica with some potassium, a composition which can be considered as quite normal. Field evidences concerning the temperature at which these fluids were active are obscure.

Experimental work designed to investigate these changes is at present in progress. It has advanced far enough to indicate, even in the very limited range of conditions so far examined, that hydrothermal change in sillimanite can be induced in the laboratory. The work has, however, not progressed sufficiently to allow any certain identification of the phase changes.

Acknowledgements.

Much of the laboratory work described in this paper constituted part of the research programme of the Division of Industrial Chemistry of the Commonwealth Scientific and Industrial Research Organization. For these results and for discussion of them the writer is indebted to his colleagues in the Cement and Ceramics Section, particularly Mr. A. J. Gaskin and Mr. H. R. Samson.

The writer also wishes to thank Dr. A. L. G. Rees and Mr. J. L.

Farrant of the Chemical Physics Section for making X-ray determinations and electron micrographs respectively.

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Connellite, buttgenbachite, and tallingite

(With Plate II)

By F. A. Bannister, Max H. Hey, and G. F. Claringbull

Department of Mineralogy, British Museum (Natural History)

THERE are many basic copper chlorides and sulphates which occur as minerals but have received little recent crystallographic study. Yet copper is a widely distributed element and many of these minerals are the products of corrosion and weathering of copper and copper ores.

In 1948 we were able to confirm the earlier goniometric work of G. F. Herbert Smith (1906) that paratacamite and atacamite are not identical species (Max H. Hey, 1950) and showed that the two minerals give different X-ray powder patterns. This result was further extended by Clifford Frondel (1950) to a single crystal and thermal study of paratacamite, in the course of which he measured the rhombohedral unit-cell dimensions and showed that this mineral can be artificially produced by various methods as well as by the action of salt-water on copper. We now find from an X-ray study of all atacamites and paratacamites labelled as such in the British Museum collections, that only one occurrence of the orthorhombic mineral itself is known in the British Isles, namely at Roughtongill.[1] It is paratacamite, not atacamite that occurs at the famous Cornish locality, Botallack mine, St. Just.

Frondel (1950) also studied copper chlorides related to paratacamite and was supplied by us with specimens not only of paratacamite itself but also of tallingite and botallackite. Frondel came to the conclusion that botallackite $Cu_4(OH)_6Cl_2.3H_2O$ is a mineral with optical properties and X-ray powder pattern entirely different from those of paratacamite and 'of other known copper minerals as far as could be determined'. He gave powder data in his paper, and we have since obtained almost identical spacings and relative intensities. So far as is known at present botallackite is a species in its own right, but we know neither its symmetry nor its crystal structure. Moreover, its formula rests upon one chemical analysis by A. H. Church (1865).

Frondel suspected, from the two specimens available to him, that tallingite is identical with paratacamite. Our own X-ray photographs of tallingite, however, showed that it should rank as an independent

[1] B.M. 31622*a*, bought of Mr. D. Lowry, 1860.

species. We therefore intended to publish powder data for tallingite as soon as we could satisfy ourselves that Church's analyses of the mineral were not analyses of a mixture of tallingite and paratacamite, the two minerals being usually closely associated.

At that time A. W. G. Kingsbury, who had been collecting many specimens from the forsaken dumps and mines of Cornwall, also suspected that tallingite was of species rank. He had enlisted the help of H. Neumann and later of J. Hartley in the Dept. of Geology, University of Leeds, to take X-ray photographs of many of his specimens and also of species he supposed to be relevant to his investigations. Most fortunately Hartley took powder photographs of connellite and found them to be identical with tallingite. This information Kingsbury generously placed at our disposal.

Connellite occurs in slender hexagonal blue prisms at many Cornish localities; Grand Central mine, Tintic district, Utah; and in Namaqualand, South Africa.[1] Powder photographs of specimens from these localities are identical (table I), and we have confirmed Hartley's identification of tallingite. We have also shown that tallingite like connellite contains sulphate as well as chloride. Our photographs are reproduced in pl. II, figs. 1 3, together with the pattern for buttgenbachite (fig. 4), which A. Schoep (1927) considered to be closely related to connellite (Hey, 1950). All the powder patterns (table I) are almost identical in the positions of the diffraction lines and their relative intensities; and all diffraction lines observed for connellite from 13·7 down to 2·29 Å. have been indexed, using the appropriate Bunn chart and the axial ratio c/a derived from our single crystal measurements. Rotation, oscillation, and Weissenberg equi-inclination photographs (pl. II, fig. 5) have been about the $c[0001]$ and $b[11\bar{2}0]$ axes of a prism of connellite from B.M. 60566, St. Day United Mines, Cornwall.[2] These confirm hexagonal symmetry and yield a simple rhomb-based cell with dimensions $a = 15{\cdot}82$, $c = 9{\cdot}14$ Å. The only systematic absences recorded for all the observed diffractions are of the type $hh\bar{2}\bar{h}l$ for l odd. Hence the space-group may be D^4_{3h} $-C\bar{6}2c$, $C^4_{6v}-C6mc$ or $D^4_{6h}-C6/mmc$; and H. A. Miers (1894) failed to detect any pyroelectricity in the mineral. The ratio c/a is exactly one-half of the value of the axial ratio $c/a = 1{\cdot}1562$ obtained for a crystal of connellite by N. Story-Maskelyne (1863) on a single-circle goniometer. Based upon our axial ratio obtained by X-ray measurements Maskelyne's form $(10\bar{1}1)$ now becomes (2021).

[1] Also at Bisbee, Arizona, but no specimen is available to us for X-ray or chemical study.

[2] Probably from the C. F. Greville collection, purchased 1810.

TABLE I. X-ray powder data for connellite, buttgenbachite, and tallingite in Å.

hkil	d_{calc}	Connellite.		Buttgenbachite.		Tallingite.	
		I	*d*	*I*	*d*	*I*	*d*
$10\bar{1}0$	13·70	vvs	13·70	vvs	13·70	vvs	13·20
$11\bar{2}0$	7·90	vvs	8·00	vvs	7·95	vvs	8·00
$20\bar{2}0$	6·85	vvw	6·90	—	—	—	—
$20\bar{2}1$	5·48	m	5·51	mw	5·51	m	5·53
$21\bar{3}0$	5·18	ms	5·20	ms	5·20	s	5·20*
0002	4·57	m	4·59	m	4·59	m	4·59
$30\bar{3}0$	4·57						
$10\bar{1}2$	4·34	m	4·35	mw	4·35	m	4·32
$11\bar{2}2$	3·97	vw	3·98	vw	3·98	vvw	3·98
$22\bar{4}0$	3·97						
$31\bar{4}0$	3·80	m	3·82	m	3·82	m	3·82
$20\bar{2}2$	3·80						
$21\bar{3}2$	3·43	m	3·48	m	3·44	m	3·42
$30\bar{3}2$	3·23	vs	3·27	s	3·27	vs	3·22
$10\bar{1}3$	2·97	vw	2·96*	vw	2·93*	vvw	2·98*
$22\bar{4}2$	3·00						
$32\bar{5}1$	2·97						
$41\bar{5}0$	3·00						
$41\bar{5}1$	2·84	vw	2·85	vvw	2·85	—	—
$50\bar{5}0$	2·74	vvs	2·75	vvs	2·75	vvs	2·74
$32\bar{5}2$	2·59	ms	2·62	m	2·61*	ms	2·61
$50\bar{5}1$	2·62						
$33\bar{6}0$	2·64						
$42\bar{6}0$	2·59	m	2·59	—	—	—	—
$41\bar{5}2$	2·50	s	2·51	s	2·51	s	2·51
$51\bar{6}0$	2·46	vvw	2·46	vvw	2·47	—	—
$51\bar{6}1$	2·37	w	2·38	w	2·38	vvw	2·38
$50\bar{5}2$	2·35						
$60\bar{6}0$	2·28	vvs	2·29	vvs	2·30	vvs	2·28*
		mw	2·25	mw	2·26	—	—
		mw	2·20	mw	2·20	mw	2·19
		w	2·09	vw	2·10	vw	2·09
		w	2·04	vw	2·05	vw	2·03
		mw	1·98	mw	1·98	mw	1·98
		vw	1·91	vw	1·92	vvw	1·91
		vw	1·855	vvw	1·861	vvw	1·853
		mw	1·811	mw	1·811*	mw	1·804
		mw	1·799	—	—	—	—
		ms	1·754	m	1·760	mw	1·756
		vvw	1·725	vvw	1·730	vvw	1·723
		vw	1·673	vw	1·680	vvw	1·674
		vvw	1·644	vvw	1·649	vvw	1·642
		vs	1·613	vs	1·621	vs	1·613
		m	1·580	m	1·587*	m	1·578
		w	1·546	vw	1·549	w	1·546
		vw	1·520	vvw	1·520	vvw	1·516
		s	1·488	ms	1·488*	s	1·488
		vvw	1·464*	—	—	—	—
		vw	1·443	—	—	vvw	1·440
		w	1·419	w	1·422	vw	1·417
		mw	1·392	mw	1·399	mw	1·392
		vw	1·371	vw	1·377	vw	1·371
		w	1·354	vw	1·356	vw	1·353
		vvw	1·333	vvw	1·333	vvw	1·333
		ms	1·313	ms	1·305	ms	1·312

Order of decreasing intensity: vvs, vs, s, ms, m, mw, w, vw, vvw. Broad lines are asterisked.

The cell dimensions of connellite, tallingite, and buttgenbachite are within the errors of determination with small cameras identical. Moreover, single crystal photographs of connellite and buttgenbachite about the c[0001] axis are superposable. It is clear that, as H. Buttgenbach (1926) suggested, connellite and buttgenbachite are isomorphous; it is an unusual type of isomorphism, SO_4'' being replaced by $2(NO_3')$, a replacement that is presumably possible because SO_4'' is only a minor, though essential, constituent.

TABLE II. Unit-cell contents of connellite and buttgenbachite.

	A	B	C	C*	D	E	F	G	G*
Cu''	36·4	38·5	39·3	37·8	37·6	37·6	35·8	36·1	37·1
Cl'	8·4	7·2	9·0	8·6	7·8	8·1	8·2	6·8	7·0
SO_4''	2·4	1·7	1·6	1·5	1·6	1·95	—	—	—
NO_3'	—	—	—	—	0·5	0·2	—	4·0	4·1
H_2O	38·3	36·0	36·2	34·8	38·8	38·0	—	38·6	39·7
Sp. gr.	3·364	3·396	3·54	—	—	—	—	3·33	—

A Connellite. Camborne, Cornwall. S. L. Penfield, 1891. Analysis on 0·074 gram.
B Connellite. Calumet and Arizona mine, Bisbee, Arizona. C. Palache and H. E. Merwin, 1909. Analysis on 0·73 gram of selected material.
C 'Ceruleofibrite'. Bisbee, Arizona. E. F. Holden, 1922, with corrections, 1924. Water by difference.
C* Holden's analysis recalculated assuming a specific gravity of 3·41.
D Connellite. Czar mine, Bisbee, Arizona. W. E. Ford and W. M. Bradley, 1915. Specific gravity assumed to be 3·41.
E Connellite. Grand Central mine, Eureka, Tintic district, Utah. W. E. Ford and W. M. Bradley, 1915. Specific gravity assumed to be 3·41.
F 'Footeite'. Copper Queen mine, Bisbee, Arizona. G. A. Koenig, 1891. Analysis on 0·0165 gram; SO_3 not tested for, but later shown to be present in the type material.
G Buttgenbachite. Likasi, Belgian Congo. A. Schoep, 1925.
G* Schoep's analysis recalculated assuming a specific gravity of 3·424.

Owing to the small percentage of SO_4'' present, to the rarity of the mineral, and to the frequent presence of other copper minerals accompanying it, the chemical formula of connellite is still in doubt. We have calculated the empirical unit-cell contents for all the available analyses accompanied by specific gravity determinations, and obtain the results in columns A–C of table II; these show a marked variation in all constituents, and by themselves would leave the formula still in doubt. But it will be noted that the observed specific gravity for Holden's analysis C (1922) is in marked disagreement with the other two; we therefore redetermined the specific gravity of connellite, using the same Cornish specimen[1] (B.M. 60566) as was used for the determination of unit-cell

[1] This specimen was tested for sulphate and nitrate and was found to contain sulphate only.

dimensions, and obtained the value D_4^{18} 3·41±0·01, in close agreement with Palache and Merwin (1909) and fairly close agreement with Penfield (1891). Adopting this new value for the specific gravity of connellite, a recalculation of Holden's analysis gives C*; two analyses by Ford and Bradley (1915), in which account was taken of the possible presence of nitrate but no specific gravity was determined, give D and E when combined with our specific gravity and cell-size determinations, and an old, incomplete analysis by Koenig (1891) of footeite gives F (footeite was shown to be identical with connellite by Ford and Bradley).

We next proceeded to calculate the unit-cell content of buttgenbachite (table II, col. G), using Schoep's analysis and specific gravity, and we were surprised to find that the copper content was apparently lower than for connellite. Suspecting that Schoep's specific gravity might be in error, we redetermined the specific gravity on a type specimen[1] (B.M. 1933,267), and obtained the much higher value $3{\cdot}42_4 \pm 0{\cdot}01$, leading to the unit-cell contents given in table II, col. G*.

Remembering that the possible space-groups for connellite and buttgenbachite have only even numbers of equivalent positions, it is evident that the unit-cell contains $38Cu^{\cdot\cdot}$, $8Cl'$, and $2SO_4''$ or $4NO_3'$, but the water content is less certain. Most of the analyses suggest $38H_2O$, but the calculated specific gravity for this formula is distinctly higher than that observed, both for connellite and buttgenbachite, and the careful analysis of Palache and Merwin, on specially selected material, suggests $36H_2O$, which gives a calculated specific gravity nearer to the observed value.

In table III the analyses of table II are compared with the calculated percentage compositions and specific gravities for the two possible pairs of formulae:

Connellite: $2[Cu_{19}Cl_4SO_4(OH)_{32}.2$ (or perhaps $3)H_2O]$

Buttgenbachite: $2[Cu_{19}Cl_4(NO_3)_2(OH)_{32}.2$ (or perhaps $3)H_2O]$

It remains to consider the nature of Church's tallingite (1865), which our X-ray study has shown to belong to the connellite-buttgenbachite group. Chemical tests showed that the blue crusts of tallingite contain sulphate; nitrate is either absent or quite small in amount. Tallingite is therefore an impure connellite.

The original tallingite analysis shows CuO 66·24 %, Cl 11·33 %, and Church mentioned in a footnote that a little sulphate was present among other impurities; he assigned this sulphate amounting to 0·3 % SO_3, to

[1] This specimen was tested for sulphate and nitrate and was found to contain nitrate only.

gypsum. This sulphate we now presume to have come from the connellite. The Cu : Cl ratio is 2·6, while in paratacamite it is 2, and in connellite 4·75. The material analysed was probably mainly paratacamite

TABLE III. Comparison of analyses with calculated percentage compositions of connellite and buttgenbachite.

	A	B	C	D	E	F	G	Connellite. $4H_2O$	Connellite. $6H_2O$	Buttgenbachite $4H_2O$	Buttgenbachite $6H_2O$
CuO	72·3	75·96	73·8	73·38	73·41	71·7	71·56	74·62	73·96	73·60	72·97
Cl	7·4	6·37	7·5	6·82	7·05	7·1	6·02	7·00	6·94	6·91	6·85
SO_3	4·9	3·43	3·6	3·15	3·84	—	—	3·95	3·95	—	—
N_2O_5	—	—	—	0·72	0·30	—	5·40	—	—	5·26	5·21
H_2O	17·2	16·07	15·04	17·13	16·81	—*	17·34	16·01	16·75	15·79	16·52
Sum*	100·1	100·41	99·67	99·7	99·82	—	99·04	100·00	100·00	100·00	100·00
Sp. gr.	3·364	3·396	3·54	—	—	—	3·33	3·396	3·426	3·443	3·473

* After deduction of O for Cl.

Columns A–G correspond to A–G of table II. In the last four columns are given the calculated compositions and specific gravities for connellite and buttgenbachite assuming 4 or 6 molecules of water (exclusive of hydroxyl water) per unit cell.

with perhaps 10–20 % of connellite and 5 % or more of adsorbed water. The fibrous to enamel-like crusts of tallingite are obviously by no means uniform, and vary in colour from a greenish-blue to a deep royal blue; this darker material was also analysed by Church, who described it as another new copper chloride, more basic than tallingite, but he did not give it a new name and it has always been classed in mineral collections as a variety of tallingite. Church's analysis of this dark blue variety shows 67·25 % CuO, and 8·73 % Cl, a Cu : Cl ratio of 3·4, which would correspond to a mixture of about equal quantities of paratacamite and connellite; again, the water content is very high, and Church's analysis, giving nearly 5 % lost in vacuo at room temperature, shows that much of it is adsorbed. On all the specimens the dark blue connellite is very closely associated with lighter coloured material, and it is evident that Church was unable to isolate the connellite for analysis.

We wish to acknowledge the enthusiastic assistance of Mr. C. W. Hamley and Mr. D. L. Williams, also of the Department of Mineralogy, British Museum (Natural History).

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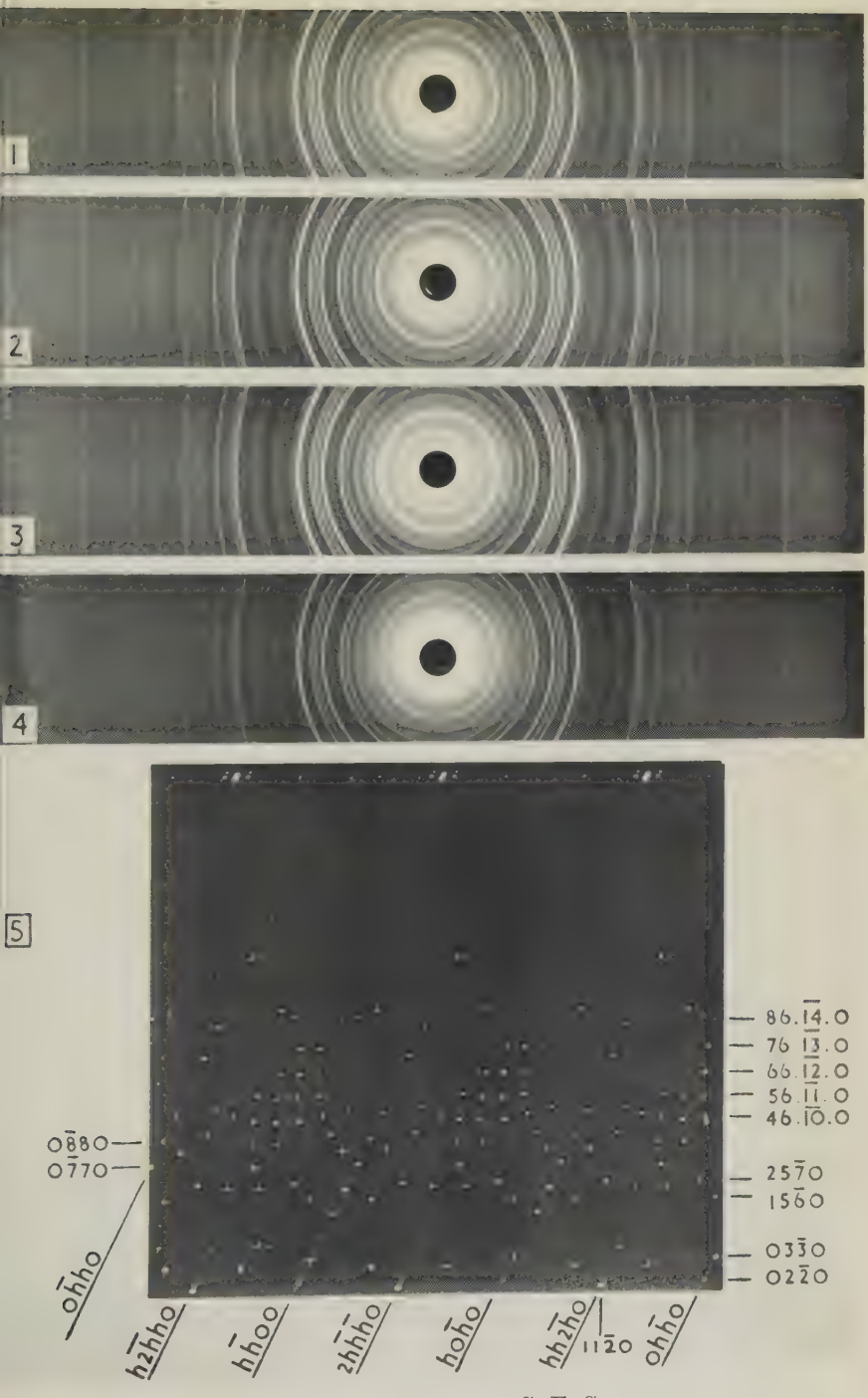
Explanation of Plate II

Figs. 1–4. X-ray powder photographs in 6 cm. diameter camera, Cu-$K\alpha$ radiation ($\lambda = 1{\cdot}542$ Å.).

1. Connellite, from Concordia mine, Namaqualand, South Africa. B.M. 32446.
2. Connellite, from St. Day United mines, Gwennap, Cornwall. B.M. 60566.
3. Tallingite, from Botallack mine, St. Just, Cornwall. B.M. 36530.
4. Buttgenbachite, from Likasi, Katanga, Belgian Congo. B.M. 1933,267.

Fig. 5. Zero-layer, normal beam, Weissenberg X-ray photograph about [0001] of connellite crystal from St. Day United mines, Gwennap, Cornwall. B.M. 60566; 6 cm. diameter camera, Cu-$K\alpha$ radiation.



F. A. Bannister, M. H. Hey, and G. F. Claringbull:
Connellite, buttgenbachite, and tallingite

An X-ray study of schultenite

By G. F. Claringbull

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In 1926 schultenite from Tsumeb, Otavi, South-West Africa, was described as a new mineral by L. J. Spencer[1] and related to the compound $PbHAsO_4$. The specimen on which the original description was based is still unique in the British Museum collection and was used for the present study. There appears to be no record in the literature that the mineral has been discovered in any other locality.

For the X-ray examination rather small fragments (less than $0{\cdot}1 \times 0{\cdot}05$ mm.) were broken from pieces of crystals since all the available crystals were too large and the material has a high absorption to X-rays. Single crystal rotation, oscillation, and Weissenberg photographs in 6-cm. diameter cameras with Cu–$K\alpha$ radiation as well as Laue photographs (crystal-plate distance 4 cm.) with tungsten radiation were used to derive the unit-cell dimensions and space-group.

With a crystal fragment oscillated about an axis normal to the (010) cleavage face the presence of a symmetry plane parallel to (010) was confirmed and the unit-cell edge b determined from the layer-line distance. Zero, first and second layer-line equi-inclination Weissenberg photographs about the same axis gave approximate values for the unit-cell edges a and c and showed that the only systematic absences are $h0l$ with h odd leading to the space-groups C_s^2—Pa or C_{2h}^4—$P2/a$. More accurate unit-cell dimensions were subsequently obtained by measurements of indexed high-order reflections on the equatorial layer-lines of rotation photographs about the axes b and c. The angle β was measured from a Laue photograph of a crystal fragment of schultenite accurately set normal to (010) which also served to confirm the suitability of the chosen axes a and c (those of Spencer). The value of $180° - \beta$ so obtained $84\frac{1}{2}°$, is in good agreement with that determined by goniometric means $84°\ 36'$. Weissenberg photographs were also taken about the axis c.

The unit-cell dimensions for schultenite are therefore: a 5·83, b 6·76, c 4·85 Å., β $95\frac{1}{2}°$ giving the volume of the unit-cell 190·4 Å.^{3}; space-group Pa or $P2/a$. Assuming that the theoretical formula is $PbHAsO_4$ and

[1] L. J. Spencer, Min. Mag., 1926, vol. 21, pp. 149–155.

using the density 5·943 determined by Spencer, the number of molecules in the unit-cell is found to be 2 (calculated value 1·96).

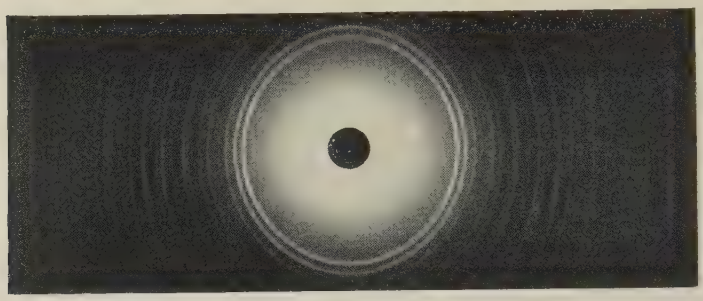


Fig. 1. Powder pattern of schultenite taken in 6 cm. diameter camera, Cu–$K\alpha$ radiation (λ=1·542 Å.).

The axial ratios calculated from the unit-cell dimensions are

0·862 : 1 : 0·717

and compare satisfactorily with the goniometric values

0·8643 : 1 : 0·7181 (L.J.S.)

A powder photograph (6 cm. diameter camera Cu–$K\alpha$) (fig. 1) of a specimen prepared by grinding up crystal fragments in an agate mortar was measured with the results shown in Table I. Almost unambiguous indexing down to 2 A. has been found possible by calculating spacings from the single crystal data and checking the powder diagram against indexed single crystal rotation photographs. Powder data for the artificial compound[1] are in good agreement with the stronger lines of the schultenite pattern.

In the time available it has not been possible to work out in detail the crystal structure of the mineral, but a rough model of a possible structure which appears to be in reasonable accordance with inspected intensities of the principal diffraction spectra has been constructed from space-group and crystal chemical considerations. It is intended to provide more complete data in the future.

In the more symmetrical of the two possible space-groups there are six sets of twofold special positions, four at the centres of symmetry and two on twofold axes, available for the lead and arsenic atoms. Of the $hk0$ reflections all those with h odd are weak and this precludes the

[1] Published by the American Society for Testing Materials, the American Crystallographic Association, and the (British) Institute of Physics, Joint Committee on Chemical Analysis by X-ray Diffraction Methods, Philadelphia, 1950: card no. 1488.

possibility of heavy atoms residing at the centres of symmetry but is in agreement with their being on twofold axes. It was also assumed that the oxygens are arranged tetrahedrally about the arsenics and a scale

TABLE I. X-ray powder data for schultenite.

hkl	*d* calc.	*I*	*d* obs.	*I*	*d* obs.
010	6·76Å.	mw	6·7Å.	w	1·643
001	4·83	vw	4·80	w	1·617
110	4·40	mw	4·37	vw	1·568
011	3·93	vvw	3·93	ms	1·546Å.
020	3·38	vvs	3·35	mw	1·522
11$\bar{1}$	3·38			mw	1·474
111	3·13	vs	3·13	vw	1·452
200	2·90	mw	2·90	vw	1·430
021	2·77	vw	2·76	vvw	1·411
210	2·67	vw	2·66	vw	1·393
20$\bar{1}$	2·60	vvw	2·58	vw	1·377
12$\bar{1}$	2·55	m	2·55	vw	1·348
121	2·45	w	2·42*	vw	1·330
002	2·41			w	1·297
211	2·25	w	2·24	w	1·276
030	2·25			vw	1·251*
220	2·20	ms	2·19	mw	1·224
11$\bar{2}$	2·185			mw	1·212
130	2·10	vw	2·10	vvw	1·197
112	2·06	mw	2·05	vw	1·180
031	2·04	vvw	2·04	vvw	1·168
		s	1·950*	vw	1·158
		mw	1·899	vvw	1·140
		w	1·859	vw	1·126
		vvw	1·820	vvw	1·110
		s	1·778*	vw	1·092
		ms	1·683	vw	1·080
		(continue next column)		vw	1·074

Order of decreasing intensity: vvs, vs, s, ms, m, mw, w, vw, vvw; broad lines are asterisked.

model of a close-packing type was constructed in which the lead and AsO_4 groups were mounted on wires representing the twofold axes. It was found possible with this model by putting lead atoms on one set of twofold axes and AsO_4 groups on the second set to arrange them in fulfilment of the space-group symmetry within the available cell space. In this arrangement (fig. 2) the lead atoms are in eightfold coordination and with y coordinates Pb = 0·80 and As = 0·21 an approximate agreement with observed intensities is achieved. A feature of this model is the layering normal to the b axis which if confirmed may be related to the extraordinarily good cleavage on (010). My thanks are

due to Dr. F. A. Bannister for suggesting an examination of this mineral.

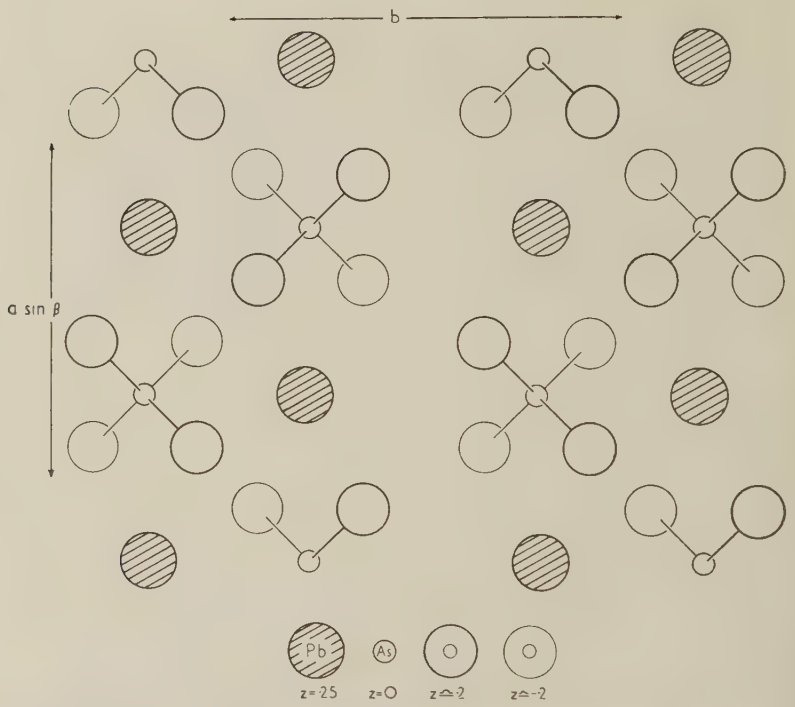


FIG. 2. View along *c*-axis of proposed crystal structure for schultenite ($PbHAsO_4$); positions of hydrogens not shown.

The uranium deposits of the Tete district, Mozambique

By C. F. Davidson and J. A. E. Bennett

Geological Survey of Great Britain.[1]

Introduction.

EARLY in 1947 an unusual mineral deposit was discovered at Mavuzi in the Tete district of Mozambique. The discovery was made by native boys searching for corundum on behalf of Senhor Mario Canuto de Carvalho, a Goanese prospector who had for some years been associated with primitive gold and corundum operations on the north bank of the Zambesi. The dominant ore-mineral in the new deposit was superficially similar to the pegmatitic samarskite found in small quantities in the mica-mining districts of the Alto Ligonha in eastern Mozambique; and when exposure of the mineral to a photographic plate confirmed that it was radioactive, the identification as samarskite was accepted both by local prospectors and by most of the field geologists who later worked on the deposits. The presence of uranium in the ore was first proven in a chemical analysis by the Southern Rhodesian Geological Survey.

Within a few months of the first discovery, on which concession rights were granted by the Portuguese Colonial Government, some 50 tons of concentrated mineral assaying between 7·5 and 8·0 % U_3O_8 had been recovered from the principal prospect. A year later more than 300 claims, each a kilometre in radius, had been staked for uranium. Options on the main properties were taken up jointly by the British South Africa Company, New Consolidated Gold Fields Ltd., and Gold Fields Rhodesian Development Co., Ltd., and exploratory development was actively pursued.

In June and July 1947 specimens of the ore were submitted to the Geological Survey in London by the Southern Rhodesian Geological Survey, by various London dealers in rare minerals, and by certain British mining houses. The first specimens received were analysed for uranium only, giving values of from 7 to 10 % U_3O_8; and from its appearance the mineral was assumed to be a euxenite or samarskite as was reported by the senders. Samarskite is of frequent occurrence

[1] Communicated by permission of the Director.

in the Mozambique pegmatites, no less than eleven mining concessions taken out from 1935 to 1939 mentioning this mineral by name; but as the output had hitherto been insignificant the new occurrence did not arouse as much interest as it might have done had the true nature of the mineral been recognized earlier. Not until a reliable chemical analysis became available, showing very high titanium and a complete absence of niobium and tantalum, was it realized that the mineral was almost a unique species. It has approximately the composition of an ilmenite with some 8 % urania. Investigations by Dr. F. A. Bannister of the British Museum (Natural History) and by Mr. J. E. T. Horne of the Geological Survey, already published in the *Mineralogical Magazine* (1950), have shown that the mineral is essentially identical with davidite, a species which occurs in very sparse amounts at the Radium Hill uranium workings, South Australia. In Mozambique a few crystals of this hitherto very rare mineral have been found weighing as much as 40 or 50 lb.

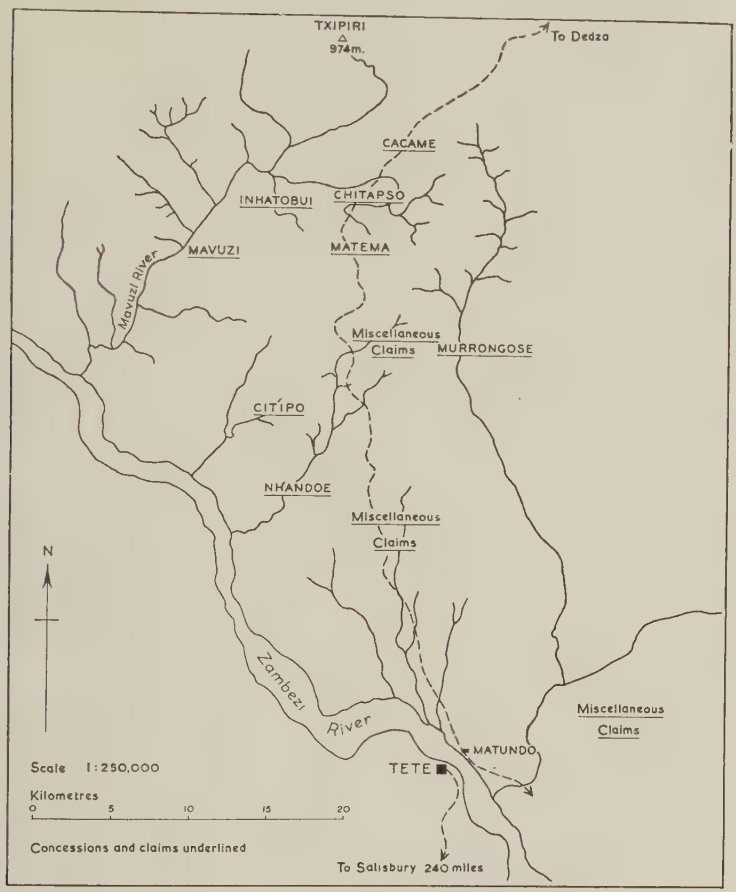
Following this preliminary mineralogical work the authors were invited by the British South Africa Company to make a brief field study of the deposits, and in June–July 1948 a full investigation of the various prospects was undertaken in conjunction with Dr. R. A. Pelletier (Chief Geologist) and Mr. A. T. M. Mehliss (Resident Geologist) of New Consolidated Gold Fields. It was found that the uranium complex was of a completely new geological type, but that the extent and importance of the deposits had been greatly exaggerated, the reserves of economically workable ore being quite insignificant viewed from the strategic and supply aspects. The British control of the deposits was allowed to lapse in August 1948. Since then close on another 100 tons of davidite has been produced by Portuguese operators at a high cost, principally from float and hand-cobbed surface ore, and has found a market in France.

The present paper presents a brief description of the geology and mineralogy of the occurrences. In the course of the field studies the authors had the benefit of constant consultation with Dr. Pelletier and Mr. Mehliss, and without the collaboration and assistance of these gentlemen this report could not have been produced.

Topography, Climate, and Vegetation.

The Discovery Concession is situated on the Mavuzi river, a tributary joining the Zambesi on its north bank at a distance of about 30 miles from Tete, the administrative centre of this part of Portuguese East Africa. The Mavuzi mine is reached from Tete by ferry across the

Zambesi to Matundo, thence by the main all-weather road for 21 miles to Matema, and thence by a 9-mile bush road.



SKETCH MAP OF URANIUM CLAIMS, TETE DISTRICT, MOZAMBIQUE.

FIG. 1.

According to official climatic maps the Mavuzi district is the hottest spot in Africa south of the equator. The mean annual temperature observed in 1947–48 was 83° F., occasionally falling to under 40° F. at night in winter and in the summer rising to 110° F. Rainfall averaged some 34 inches in the year. The climate is not healthy and malaria is endemic.

The region is part of the Zambesi valley, and is topographically a maturely dissected peneplain which has suffered recent rejuvenation of

drainage. The mineralized country is rugged, being cut by innumerable steep-sided ravines, some of which contain perennial streams. Although over 300 miles from the coast, the altitude is only about 350 feet above sea-level. Bed-rock is not well exposed and the considerable depth of rock-decomposition products is a serious handicap to geological studies. The vegetation consists of grass up to 6 feet high and open mopani bush, the latter providing a fair reserve of mine timber. Occasional baobab trees are a striking feature of the landscape.

Geology.

Prior to the present investigation, practically no regional geological work had been carried out in the Mavuzi district. The only map available (Borges, 1946) is a geological sketch on a scale of 1 : 1,000,000, which indicates that the principal feature of the district is a roughly oval-shaped intrusion of gabbroic composition some 80 miles long by 30 miles broad. This is overlain by sediments of Karroo age except on its north-west side, where gneisses and granites are said to occur. Apart from frequent basic dikes of roughly east–west trend and probably of Tertiary (Rift Valley) age, the basic igneous masses are all of pre-Karroo age and are probably all pre-Cambrian. So far as is known, the radioactive minerals are only found within the outcrop of the gabbro mass.

The gabbro is of noritic type, akin to a basic charnockite, the constituent minerals being dominantly labradorite and hypersthene. The grain-size varies greatly and is often very coarse. Anorthositic phases consisting essentially of labradorite felspar are frequent and are usually coarse in grain. This complex was intruded by northerly-trending basic dikes, the emplacement of which was followed by intensive shearing in a north–south direction. Later acid intrusions, including syenitic dikes and quartz veins, are accompanied by some larger masses of syenitic rock occurring typically in dike-like and lenticular forms. Coarse-grained pegmatites of quartz and potash-felspar also penetrate the basic complex, and are sometimes injected in lit-par-lit fashion into sheared epidioritic modifications of the norite. The final igneous activity in the district is seen in the dikes of east–west trend that are clearly much later than the rest of the complex. No true granites were seen anywhere in the region; they are absent from the assembly of boulders in the bed of the Mavuzi river which, since good exposures of fresh rock are lacking over much of the area, provides the best representation of the local lithology.

A number of what are apparently roof-pendants and enclaves of an ancient sedimentary complex are found within the norite-anorthosite mass. These include principally limestones and more rarely pelitic and psammitic schists, the schistose rocks sometimes containing lit-par-lit injections of granite-pegmatite. The most notable of these enclaves, seen at the Matema lime quarry, 9 miles east of Mavuzi, is a pendant or xenolith of crystalline limestone about 200 yards wide by over a mile long. The limestone is relatively pure and free from calc-silicates, exhibiting only a little scapolite, phlogopite and albite arranged in well-defined bands. No traces of uranium mineralization were detected in Geiger-counter investigations over this well-exposed body of limestone.

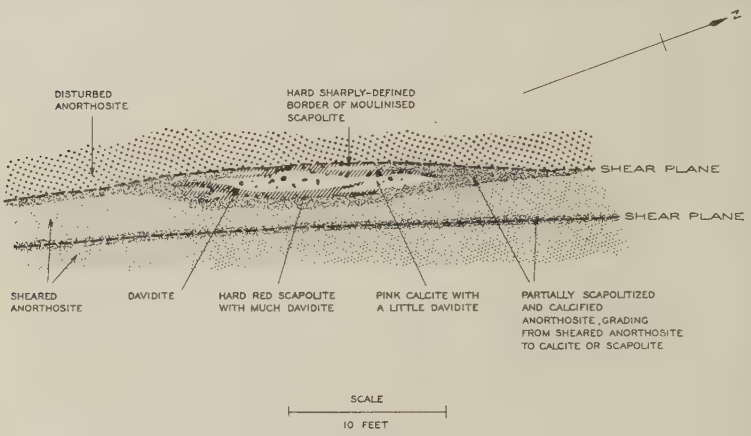
Mineralization.

The uranium mineralization is patchily distributed over an area of about 300 square miles, but the wide extent of this distribution is no indication of the amount of mineral involved. Throughout this region claims were staked with the utmost liberality wherever scattered mineral float or a mineralized outcrop was encountered, entirely without regard to the prospects of mineralization continuing in depth. Some of the properties contain no more than traces of davidite, a fair proportion of the mineral collected by some claim-holders being magnetite. At the time of our visit in mid-1948 all the claims had been prospected on a very limited scale by trenching—probably upwards of 500 trenches in all, mostly sited at random without reference to the geological structure. Only at the Mavuzi property worked by the British companies had any scientific development been carried out. The concession of Inhatobui adjoining Mavuzi to the north-east, on which some 250 exploratory trenches had been dug, and the Citipo claims some 10 miles south-east of Mavuzi, both proved to be of mineralogical interest.

The associations of the radioactive mineral davidite show considerable variety, but four different and distinctive types of gangue are found. These consist of scapolite, calcite, pyroxene, and a 'felsitic' rock. The mineralization is for the most part intimately associated with shear zones, the largest of which (at Mavuzi) is about half a mile in length, with a width of from 5 to over 40 feet. The shears have converted the noritic country-rocks to strongly-foliated epidiorites, frequently exhibiting augen structure, in which there has been very extensive scapolitization of the felspar.

Following the consolidation of the basic rocks the complex was locally subjected to intense shearing stresses, the finer-grained norites being

transformed to epidiorites and the coarser rocks to streaky hornblende-gneisses of basic composition, often with a well-developed augen structure. A typical epidiorite shows in thin section sheaves of hornblende prisms in a matrix of granular scapolite, associated with a varying



TYPICAL OCCURRENCE OF DAVIDITE
IN ASSOCIATION WITH CALCITE AND SCAPOLITE
MAVUZI, TETE, MOZAMBIQUE.

FIG. 2.

quantity of granular zoisite and some epidote. As was to be expected, the earliest sign of shearing stress is alteration of the pyroxene to amphibole; but the transformation of felspar to scapolite, dating from the time of shearing or possibly a little later, is even more widespread. The Mavuzi rocks show more widespread regional scapolitization than any other igneous complex known to the writers. Scarcely a single specimen from the anorthosite-norite suite can be found that is altogether free from scapolite; and extensive shear zones, assumed in the field to consist of saussurite, have been found on laboratory study to be formed of pure scapolite rock or of scapolite-calcite rock, often with relict structures of the original norite. This extensive scapolitization extends to the deepest mine workings (110 feet) and presumably continues in depth. It is characteristic of all the ore-bearing zones and is attributed to the hypogene ore-bearing solutions. At the surface the scapolite weathers to a white clay which is commonly rich in calcite, the calcite sometimes giving rise to a pan of secondary calcrete a foot or two beneath the ground level.

The scapolite-calcite type of mineralization.—The scapolite-calcite

mineralization is the commonest development at the Mavuzi mine. Early in the mineral sequence massive white quartz seems to have been injected into the shear zones, and must have formed veins up to 2 or 3 feet wide. Disrupting the quartz, and sometimes combining with it to form a massive diopside, a high-temperature dolomite-calcite is found. Bodies of calcite and or dolomite are rather common, up to 50 feet long and 3 feet wide; but whether these are all of metasomatic origin or whether some may represent enclaves of sedimentary rock is uncertain. Locally they are relatively free from pyroxene and quartz, locally pyroxene is seen enclosing some remnants of quartz, and elsewhere quartz blocks up to 2 feet wide are to be seen, each surrounded by a reaction band of diopside. Occasionally a little cinnamon-brown chalybite is present. Certainly much if not all of the carbonate is metasomatic, for a calcifying invasion has extensively attacked the neighbouring sheared gabbros, the anorthositic phases being particularly affected. The calcite is accompanied by a very great deal of scapolite. All stages from incipient to complete scapolitization of gabbros and anorthosites, followed by partial to complete calcification, are evident at more than half a dozen localities. Pyroxene remnants are marked by cloudy chlorite and thus form palimpsests of the original rock structures.

During the emplacement of the calcite and scapolite a number of sulphides and oxides were introduced. These include pyrite, pyrrhotite, chalcopyrite, and rather frequent molybdenite, with rutile, davidite, magnetite, ilmenite, and a little tourmaline. Some golden-brown apatite is locally associated with the oxides, particularly with davidite. The highest concentrations of davidite occur in the more intensely scapolitized portions of the altered basic rocks, although a considerable amount occurs scattered throughout the massive calcite which represents the advanced stage of the emplacement process.

The scapolite-rich bands are typically narrow, seldom exceeding 2 feet in width, and they may persist in length and depth up to 50 feet, although they are usually of much smaller extent. Several narrow bands may occur grouped over a width of rock of 20 feet or so. The presence of davidite is invariably marked by pink to deep red staining, forming an aureole round the typically plum-size particles of radioactive mineral. Where the latter are abundant the whole rock assumes this red colour. Local staining is generally absent when the mineral is embedded in calcite, though the latter may also have an overall pink colour.

Subsequent to the mineralization, renewed movements gave rise to local shearing of the scapolite zones and plastic flow of the calcite. As

a result, the molybdenite flakes are oriented parallel to the direction of movement and the davidite and rutile crystals are typically shattered to pieces, often with evidence of having been dragged along to form parallel trains. Good crystal forms are therefore of rare occurrence. In field appearance the scapolite zones often have a davidite-rich core, suggesting that the scapolite-forming and davidite-bearing liquors were introduced through narrow fissures, scapolite mineralization permeating the neighbouring rocks and davidite being deposited near the fissures. The identity of these structures is sometimes preserved in the massive calcite, but elsewhere is represented by strings of scapolite remnants and davidite, and often by strings of davidite only.

Subsequent to these phases late quartz was introduced, usually in small stringers which are seen to cut both scapolite and calcite masses and break through crystals of davidite, rutile, magnetite, and apatite. The late quartz is sometimes drusy and is frequently smoky in appearance. It is associated with specular haematite, magnetite, and pyrrhotine, the decomposition of which results in locally intense iron staining. Unlike the early quartz it does not give rise to the formation of pyroxene in contact with carbonate. Very locally, late silicification has been sufficiently intense to replace completely the scapolite and calcite within an inch or so of the borders of the veinlets, thus providing the rare spectacle of davidite embedded in quartz. Late stringer veining of the altered gabbros by fibrous calcite and red stilbite is also fairly common.

The pyroxenic type of mineralization.—In this type of occurrence the davidite is associated with coarse-grained pyroxenic rocks that have the superficial appearance of basic pegmatites. Like the calcite and scapolite bodies they are lenticular in shape, up to some tens of feet in length and a few feet in width. They commonly occupy shear zones little affected by subsequent movements. This pyroxene association is well developed in the Inhatobui area, adjacent to the Mavuzi claims.

Several features indicate that the origin of these bodies is different from that of true pyroxene pegmatites. The latter may be observed elsewhere throughout the norite-anorthosite complex to consist of massive coarse hypersthene, sometimes grading into coarse hypersthene-labradorite rock. In the rocks under discussion the pyroxene is not a hypersthene but a green diopside. Crystal individuals range from an inch or so to a foot across and comprise the bulk of the rock. Subsequent movements and metasomatism have caused incipient alteration to a dark tremolite-like amphibole. Red and pink scapolite, generally mas-

sive and granular but occasionally in prismatic crystals up to an inch in length, occurs intergrown with the pyroxene. This mineral is rarely present in important quantity within the pyroxene bodies, where it usually occurs in vague, vein-like bands, but marginal concentrations are fairly common. The pyroxene-davidite assemblages are invariably accompanied by an aureole of scapolitization of the neighbouring country rock, extending for several feet on either side and decreasing in intensity outwards. In these aureoles the ferromagnesian minerals are represented by black hornblende and some tourmaline, biotite, and apatite. Another feature of this type of occurrence is the presence of late veinlets and stringers of vermiculite running parallel with the pyroxene bodies, often along their margins.

Mingled with these pyroxene bodies at Inhatobui are many small davidite-bearing scapolite—or more rarely calcite—deposits of the type previously described. Occasionally the massive pyroxene is seen to have a core of white quartz or to contain occasional blebs of quartz throughout its mass. Elsewhere white quartz seems to have entered as a late injection. Again, some pyroxene bodies were observed to have a core of massive calcite with a little scapolite round which the pyroxene forms an obvious crust.

The davidite occurs in the scapolitic phases marginal to and enclosed within the pyroxenic bodies. As before, the scapolite is invariably stained pink or red where in contact with the davidite. The mineral also occurs marginally in the infrequent massive calcite, the latter apparently derived from calcification of scapolitic zones. Davidite crystals in these associations are typically imperfect and have grain sizes varying from microscopic to rare individuals about 4 inches across.

Davidite also occurs in the vermiculite veinlets. The mica is brown biotite occurring in closely packed books up to two inches across. The veinlets vary in width from an inch to 4 inches. Scapolite is usually absent. The radioactive mineral forms grains of various sizes, exceptionally giving individual crystals 3 or 4 inches across which occupy the whole width of the veinlet.

In addition to these associations davidite occurs less frequently embedded in the massive pyroxene, usually marginally in large pyroxene individuals.

The 'felsitic' type of mineralization.—A further type of davidite occurrence is especially well developed at the Citipo claims, where the radioactive mineral is found in a hard pink-coloured rock which was termed 'felsite' in the field. Patchy developments of the same

character have been seen at Mavuzi. Microscopic examination shows that this 'felsitic' rock consists essentially of sodic plagioclase intimately associated with davidite-bearing carbonate, the davidite crystals being surrounded by the usual red staining. Quartz is absent or present in minute quantity only.

The 'felsite' or soda-plagioclase rock is of relatively late date since it is commonly found in veins (up to a foot in width) intruding the mineralized shear zones in scapolitized norite. The not infrequent occurrence of prisms of tourmaline in the felspathic rock suggests a link with the scapolitizing fluids and a possible derivation from the labradorite of the gabbro. It is noteworthy that the total amount of sodic plagioclase in these 'felsites' is never great. The larger bodies contain a considerable proportion of calcite, but in smaller masses the albite may be preponderant and thin veins of a relatively pure albite rock are found traversing masses of metasomatic limestone. All these 'felsite' bodies are characteristically impersistent, being seldom more than 20 feet in length. Grains of davidite, occasionally found scattered sporadically throughout and sometimes only of marginal distribution, may have been picked up from pre-existing rock; but they may equally well be contemporaneous with the albite-rock, which clearly marks a late phase of the pneumatolytic alteration of the norites and anorthosites and is not to be regarded as of true igneous origin.

Sequence of mineralization. The following is a reconstruction of the history of the Mavuzi complex in so far as we have been able to decipher the sequence of mineralization from field examination and from petrographic and mineragraphic study.

(1) The norites and anorthosites were sheared to epidiorite and possibly to saussurite rock, the shear-zones forming the most likely channels for later mineralizing fluids.

(2) Massive quartz was introduced into the shear zones in irregular blows. Most of this quartz was shattered by later movement.

(3) Progressive alteration to scapolite and carbonate in the shear rock took place through the influence of the mineralizing fluids, producing scapolitized epidiorites and a massive scapolite-calcite facies. The white quartz of phase (2) is found embedded in irregular masses of dolomitic calcite, each fragment having a reaction rim of diopside (now partly or wholly transformed to tremolite). All stages can be seen up to the complete replacement of the quartz by massive pyroxene.

(4) The scapolite-calcite and scapolite-dolomite associations so formed range from wide masses of carbonate rock to somewhat narrower bodies

of pure scapolite rock, with all possible intermediate associations of scapolite and calcite. These assemblages carry davidite, rutile, sphene, magnetite, ilmenite, apatite, and molybdenite, the phases rich in scapolite being particularly favourable to davidite, usually with biotite (vermiculite) in small flakes, grains of tourmaline, and less commonly sphene and rutile. The davidite concentrations are typically narrow, probably representing deposition in the immediate vicinity of a fissure. In massive calcite davidite occurs typically in bands and stringers of individual crystals, suggesting that it was formed primarily in a narrow concentration of scapolite which was later completely calcified. Tourmaline has not been seen in the massive calcite and vermiculite occurs but rarely, though rutile and less often sphene may be found in crystals up to a few inches in length. Magnetite and ilmenite are commonly associated with the davidite, not infrequently in composite aggregates. Molybdenite occurs as scattered flakes, usually where apatite is abundant. The apatite forms stringers of small prisms as well as larger irregular crystals of a reddish-golden colour, the largest crystal met with reaching over a foot in length.

(5) There is some evidence that, at this stage, white or pinkish quartz was locally intruded into the calcite bodies. The quartz ramifies through the calcite, but forms no pyroxene or amphibole by interaction. There is, apparently, no contemporaneous mineralization except possibly some albite and apatite. Later deformation, during which the calcite underwent plastic flow, caused shearing of this quartz, giving a granular crush matrix of quartz and calcite in which quartz blocks are oriented in stringers with their long axes parallel to the direction of flow. The davidite and rutile crystals were shattered and drawn out in small trains, along which the matrix is coloured a bright red. Molybdenite flakes are also oriented parallel to the flow, while diopside crystals were crushed and transformed to tremolite.

(6) A further stage is seen in the introduction of permeation zones and stringers of translucent white quartz, associated with pyrite, haematite, and apatite. This quartz invades the crushed calcite producing locally a haematitic calcite-quartz rock, usually containing some apatite. Elsewhere stringers of haematite and apatite penetrate the masses of amphibole and pyroxene. The apatite crystallizes in abundant well-formed prisms within the quartz and sometimes contains well-defined zones of haematite where it grows in association with that mineral.

(7) Later movements have resulted in a local brecciation of these silicified zones, the breccia being cemented by thin veinlets of late white

quartz, sometimes occurring in druses with the smoky pyramids of quartz overgrown with specular haematite.

Conclusion.

The present generalized account of the davidite deposits purposely omits any detailed description of the workings or of the mine geology. It will suffice to say that the Discovery Concession at Mavuzi, which is more richly mineralized than any other known property in the district, must originally have been most spectacular. The mineral occurred here as rich streaky disseminations of crystalline masses, blocks of brecciated davidite veined with calcite and scapolite seldom weighing less than several pounds. An open-cast quarry in scapolitized norite and anorthosite, 180 feet long and locally attaining a depth of 40 feet, yielded 53 tons of hand-cobbed mineral. Many of the individual crystals, all of which unfortunately were broken up, exceeded a foot in diameter.

Towards the bottom of the quarry the mineralization weakened, and the ore encountered underground on the 100-foot level all proved to be of unpayable grade. Many other shows throughout the Mavuzi district, with promising mineralization at the surface, were found to die out underground within a few feet or a few tens of feet. The distribution of davidite along the shears is clearly very patchy indeed; and the loose and running nature of the ground is a serious handicap to mining, for the extent of mineralization underground tends to vary directly with the degree of brecciation, scapolitization, and incoherence of the bedrock.

The claims staked at localities other than Mavuzi—at Inhatobui, Nhandoe, Citipo, Cacame, Chitapso, Matema, Murrongose, and elsewhere—call for little additional comment. At their worst they contain no more than a few particles of davidite in float, at the best their mineralization is not much richer than that seen in a field of uraniferous pegmatites. Near Matema, 5 miles west of the main road, the rock quarried in an exploration trench is a coarse-grained limestone resembling a skarn ore, with much granular magnetite and a good deal of well-crystallized tourmaline in the matrix. One davidite crystal was found pseudomorphing tourmaline, and well-crystallized plates of allanite up to an inch across are present in quantity. Adjoining trenches show decomposed anorthosite-norite veined by scapolite and calcite-magnetite rock; and the skarn-like limestone is therefore again assumed to be a product of the metasomatism of anorthosite.

No uranium deposit strictly comparable to the davidite occurrences

of the Tete district is known to us. The davidite of Olary in South Australia occurs in pegmatitic lodes consisting of quartz, biotite, ilmenite, and rutile, cutting paragneisses that include scapolite-schists and amphibolites (Mawson, 1944). The country rocks are in process of granitization, and a sheared aplitic soda-granite, with which the pegmatites are genetically connected, sometimes forms the wall-rock of the lodes. The intense scapolitization and carbonatization typical of Mavuzi is not found here. The only other uranium mineralization where scapolitic alteration of the wall rock has been reported (Sandberger, 1885) is found in the mesothermal pitchblende lodes of Jáchymov in Czechoslovakia; but according to Štěp and Becke (1904) the reputed scapolite is a misidentification of oligoclase-albite.

A 'titano-magnetite' uranium mineral, possibly akin to davidite, has been recorded from pegmatites in the High Pamir of Central Asia (Golubkova, 1930), but no particulars of the geology of this occurrence seem to have been published. That davidite is of more widespread distribution than hitherto realized is, however, suggested by a study of samples recently received by the Geological Survey from a pegmatite 65 miles east of Swakopmund in South-West Africa. These have been found to be rich in titanium and iron, with about 9 % urania, and to be relatively free from niobium and tantalum; after heating to destroy their metamict nature they give X-ray powder photographs closely resembling but not identical with those of the mineral from Mozambique.

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A comparison between the parageneses of Fennoscandian limestone contact minerals and those of the Alnö alkaline rocks, associated with carbonates

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PARGAS in Finland and Mansjöand and Tennberg in Sweden are the only three Fennoscandian contact metamorphic limestone occurrences of which systematic accounts have been published; in the first case by A. Laitakari (1) and in the two latter ones by the present author (2, 3). A more complete analytical programme would have been desirable, and unfortunately many of the analyses are incomplete, especially as regards the determination of the valency of the iron. Nevertheless, the available data, and a few I have been able to add later, may suffice to give us a general idea of the paragenetical and chemical differences between these Archaean mineral parageneses and those of much younger age which occur in connexion with the limestone masses associated with the alkaline occurrence of Alnö in Sweden.

What adds special interest to such a comparison is that we have here an example of two radically different behaviours of the carbonic acid during the metamorphic growth of the minerals. In the case of the Archaean limestone contacts the CO_2, bound as calcite, is at the beginning of operation a 'sleeping partner' stirred to life by the energy of an external 'active partner' which forces it to sever its connexion with the lime and imbues it with an energy of its own. On the other hand, in the case of the Permian (?) alkaline carbonatitic rocks the carbonic acid has been the acting partner from the beginning, or in any case as far back as we can trace the genesis of the ascending alkaline extrusion, while the surrounding country rocks have played the part of the sleeping partner to which the CO_2 distributed part of its energy.

When discussing the source of energy of the first-named 'active partner', the granites around Pargas, Mansjö, and Tennberg, one cannot help but get into the firing-line of the two belligerent armies: the 'magmatists' and the 'emanation-frontists'; and especially so as one of the foremost leaders of the latter has strongly advocated the granitization of the limestone at the said localities by a diffusive process at temperatures supposedly far below the fusion-point (5).

Originally the present author treated the granite both at Mansjö and Tennberg as truly magmatic at the time of its interaction with the limestone. Whether its magmatic habit was the outcome of the crystal-differentiation of a regenerated (palingenetic) mother-magma or of the direct mobilization of down-faulted sediments is of small importance; the thing that really matters is that even if the said sediments were 'stewed' in emanations from unknown depths and chewed in orogenic convulsions, the result at the time of the brecciating of the limestone was a brew with a thermal energy of its own and the consistency of a magma. How the granite has acquired its homogeneity and thermal energy and from whatever nebulous depths the emanations may have come which may have called the granite to life need not be discussed in this connexion as long as we agree that the brecciation and the contact metamorphism of the still preserved part of the limestone cannot have been contemporaneous with the 'emanation-birth' of the granite itself. No acceptable evidence to the contrary, able to explain the actually existing structural features, has been presented so far.

Before entering upon any comparison between the two types of metamorphism, however, it may be necessary to give a condensed review of the Pargas, Mansjö, and Tennberg localities. The limestone body at Pargas is part and parcel of a petrologically varying metamorphosed pack of sediments of which comparatively narrow layers of amphibolite- and pyroxene-schists are still bordering on or intercalated with the limestone. The sedimentary formation as a whole is enclosed by migmatites, consisting of gneiss and granite, from which latter pegmatite dikes have penetrated the limestones. The Mansjö occurrence is of similar type, only on a much smaller scale, while at Tennberg the limestone is a fragment without any visible connexion with other sediments and totally surrounded by a practically homogeneous granite.

The chief distinction between Pargas and Mansjö lies in the rich occurrence of pargasite as compared with pyroxene at the former place, whereas the pyroxene is the dominating femic mineral at Mansjö. At Tennberg both kinds of paragenesis occur, the former being the result of a secondary transformation of primarily formed pyroxene. On the other hand, Tennberg is singularly lacking in chondrodite, one of the most conspicuous minerals of Pargas and Mansjö, as well as in apatite, the two minerals being only accessories. While the adjoining sediments at Pargas and Mansjö to some extent obscure the metamorphic action of the granite upon the limestone, and introduce an element of doubt when tracing the movements of the different atoms or ions taking part in

the reactions, the mineral 'skarn'-zones formed around the Tennberg limestone derive their material from the granite and limestone only. In consequence we may use the Tennberg paragenesis as the most typical of its kind when making a comparison with that of the alkaline carbonatitic rocks.

When describing the Tennberg occurrence I have previously used the simile of the hedgehog. Attacked by the thermal energy of the granite the limestone has resisted annihilation by surrounding itself with a radial growth of silicate minerals of successively decreasing acidity and increased density: wollastonite (sp. gr. 2·992)—diopside (sp. gr. 3·201 - 3·375)—idocrase (sp. gr. 3·381–3·421)—grossular (sp. gr. 4·076). Before that, however, some lime must undoubtedly have been assimilated by the granite, the evidence being a conspicuous increase of the anorthite component of the plagioclases within an aureole around the limestone. This, on the other hand, must have increased the viscosity of the granite and slowed down or finally prevented the ionic movement of excess silica towards the limestone contact. This migration of silica may have been accompanied by some soda as proved by a fairly high soda content of the wollastonite and pure albite at the actual contact, and must have been counterbalanced by the emigration of lime and carbonic acid at the initial stages of the metamorphosis and of CO_2 alone from the time the 'hedgehog' began forming.

As previously shown by the present author (3), the carbonic acid, released on decomposition of the calcite, raised the oxidation ratio of the contact minerals, while the resulting carbon monoxide escaping radially through the granite moved towards regions of higher temperature and acquired increased thermal energy. This was later spent by reducing the trivalent iron of the hornblende in the granite, creating a narrow zone of hastingsite-bearing granite around the limestone. Finally the precipitation of the anorthitic felspar at some distance from the contact and the binding of silica as a solid phase in the mineral growth at the contact is supposed to have accelerated the development of a pegmatitic phase between the two. The limestone deposit at this point may be visualized as floating in a hydatogenous liquid inside a solidified or, at least, extremely viscous granite shell. The ultimate consolidation of this liquid led to the thin zone of partly pure quartz, partly a graphic intergrowth of secondary calcite, quartz, albite, topaz, and tourmaline, which separates the contact mineral shell proper from the plagioclase-diopside aureole of altered granite. Lately some scheelite has been found, too, in veins originating from this zone.

This pegmatitic end-stage must of course have developed gradually, and the accompanying concentration of volatiles, especially water, around the limestone may be taken as mainly responsible for the breaking off of the primary crystallization of wollastonite and the ensuing alternating growth of idocrase and garnet. Unfortunately the lack of a systematic control of the valency of the iron content of the minerals prevents any attempt of a co-ordination between volatiles and oxidation ratios. In table I are compiled the meagre data at our disposal. They show that, with the exception of two phlogopites, the oxidation ratio is the lowest at Mansjö, as may be expected when taking into consideration the pegmatitic and low-energy character of the local Mansjö granite. The phlogopites in question occur in the pyroxenite-mansjöite dikes, where the concentration of fluorine and water must have been exceptionally high. At Tennberg the oxidation ratios are generally higher and at Pargas they reach in most cases, except in the case of the phlogopites, maximum values.

TABLE I. Atomic oxidation ratio, $Fe^{'''}$: $Fe^{''}$, of the minerals of the Mansjö, Tennberg, and Pargas parageneses.

	Mansjö.	Tennberg.	Pargas.
Diopside	0·07	0·00–0·05	0·41
Mansjöite	0·11	—	—
Pyrallolite	—	—	0·36
Grossular	0·00–0·10	2·04	2·61
Idocrase	0·11–0·16	0·47–0·91	—
Chondrodite	0·36*	—	0·54
Phlogopite	0·45–0·76	—	0·11–2·41
Phlogopite in pyroxenite dikes ...	3·36–13·50	—	—
Biotite	0·08	—	—
Clintonite	—	—	1·18
Pargasite	0·42	0·44*	0·05–0·45
Alkali-spinel	0·29	—	—

* From a previously unpublished analysis by the present author.

Of the oxidation ratios of the minerals within the contact zone of the granite itself, metamorphosed by the interchange with the limestone, no analyses are available, the only guidance being the approximate compositions as deduced from the optical data and some rock analyses. The hastingsite character of the amphibole around Tennberg has already been emphasized as evidence of reducing atmosphere in the vicinity of the contact. The pyroxene-gneiss, which at Mansjö replaces the amphibolite at the tapering ends of the limestone layer, shows an atomic oxidation ratio of 0·09 against 0·11 for the amphibolite; and that of the Mansjö granite drops from 0·03 to 0·00 at the contact. At Pargas the

'lime-gneiss', which according to Laitakari adjoins the limestone, consists mainly of diopside and plagioclase and shows a very low oxidation ratio of 0·03. It grades outwards into amphibolites, however, of ratios ranging up to 0·86.

We may now turn to the parageneses of the alkaline limestones. Since the report on the alkaline rocks of the alkaline district of Alnö was published two years ago by the present author (4), the minerals have been subjected to continued research, partly in order to collect more evidence sustaining the petrogenetic hypothesis presented in the above-mentioned paper, and partly to fill a gap in our general knowledge of the composition of the minerals occurring in a well-defined alkaline rock suite. More than 60 new analyses have been executed and will give the base for a systematic account of the mineralogy of this region to be published next year. They furnish at the same time interesting data for a comparison with the previously treated Archaean parageneses. Before pointing out, however, conformities and differences we may shortly recapitulate what is known about the origin of the alkaline parageneses.

As previously emphasized, the active carrier of the energy is here the carbonate, which at about a depth of 6 miles below the erosion surface at that time forced its way upwards in the shape of a liquid of dolomitic composition rich in CO_2 and F. It was suggested by the present author that the gradual change to a calcitic carbonate at a depth of 2 miles resulted from a metasomatic exchange between the liquid carbonate and the solid wall-rocks, producing a desilication of the latter and a silication of the carbonatitic magma.

In consequence we have to deal with two different types of mineral parageneses: the one of the wall-rocks and the other of the intrusive. The latter in turn may be subdivided into four main groups, viz. those of the deep-seated rocks: alnöites, kimberlites, ouachitites, and beforsites; those of intermediate depths (3–4 miles): jacupirangites and vibetoides; and those at the focal depth of the first shattering brecciation of the overlying rocks (2 miles): sövites, alvikites, nepheline-syenites, and foyaitic dikes. One must, however, keep in mind that there is no sharp limit between the different subdivisions, but that they grade into each other as follows: alnöites → kimberlites → beforsites → alvikites and jacupirangites → vibetoides → nepheline-syenites → sövites.

The ionic flow across the intrusion contact is characterized by the movement of CO_2, OH, F, Ti, Ca, P, Ba, and K into the wall-rock and Si and Na in the opposite direction. This is quite the opposite of what

took place at Tennberg, where the silica and soda moved away from the source of energy and not towards it. If, however, we look at the phenomenon from a reaction viewpoint we find that in both cases the lime attracts the silica and soda irrespectively of its being the 'active' or the 'sleeping partner' of the metamorphosis, whereas the carbonic acid, liberated at the dissociation of the carbonate (or carried as such by the magmatic solution), behaves differently in the two cases. Set free at the Archaean limestone contacts at a temperature at which it carries a minimum of acquired energy, its oxidation power will necessarily be at the beginning very low but will increase as it moves towards the source of energy, viz. the granite. The resulting carbon monoxide will then acquire more thermal energy and exercise a reducing action on the femic minerals of the granite. This is quite in accordance with what may be deduced from the scanty data of the oxidation ratios of the Archaean contact occurrences.

On the other hand, the CO_2 of the Alnö carbonatite, charged from the beginning with the high thermal energy of the volcanic vent, may be expected to exercise a much stronger oxidizing influence on the minerals of the wall-rock, especially as its internal pressure at the same time must be supposed to have been very much higher than at a simple contact between fluid granite and solid limestone, where there should be plenty of room for the gas to escape through the granite.

As, however, the carbon dioxide is travelling in a direction away from the source of energy, its oxidizing power may be supposed to weaken fairly quickly. At the same time the carbon monoxide, resulting from the oxidation, will not carry enough energy but be chemically dead and unable to create any reduction zones within the migmatites constituting the wall-rocks. The adiabatic cooling of the gases, CO_2, F, and H_2O, will contribute to putting a comparatively early limit to the distance within which metasomatic reactions could take place. In other words, the depth of the fenitization zone depends largely upon the original energy (temperature + pressure) of the hyper-fusibles of the alkaline intrusion, and the minerals may be expected to show a radial reduction of oxidation values.

The oxidation of the minerals within the alkaline rocks of the intrusion may also, in consequence, be expected to stand in a certain relation to the dissociation of the carbonate, viz. to the presence of free carbonic acid. This means that the deep-seated dolomitic dikes should show comparatively low ratios and the rocks at the upper 'explosion'-focus, sövites and nepheline-syenites, comparatively high ones. This is verified

and borne out by the compilation of the oxidation ratios of the new mineral analyses, presented in table II. The highest average values are found in the nepheline-fenite, closely followed by those of the ultrabasic

TABLE II. Atomic oxidation ratio, $Fe^{...}$: $Fe^{..}$, of the minerals of the Alnö parageneses.

	Sövites and alvikites.	Pyrochlore-bearing sövite dike.	Nepheline-syenites, dikes included.	Ultrabasic alkaline rocks.	Alnöites and kimberlites.	Beforsites.	Ouachitites.	Nepheline-fenites, inner zone.	Nepheline-fenites, outer zone.
Andradite	—	—	2·50	—	—	—	—	5·25	—
Melanite	—	—	3·21	3·12–5·16	—	—	9·44	—	—
Aegirine-augite ...	0·63–2·17	2·44	0·89–1·03	0·85–1·55	—	1·56	—	2·56	0·70–1·02
Hornblende ...	—	—	—	1·59	0·65				
Serpentine	—	2·92	—	—	—	—			
Phlogopite	1·15	1·96	—	—	—	—	—	—	—
Biotite	0·20–0·82	—	—	0·89	0·37	0·40	—	—	—
Soda-orthoclase ...	2·50	—	4·55–5·50	—	—	—	—	9·10–0·00	3·42
Altered felspar* ...	—	—	—	—	—	—	—	4·50–4·94	2·23–3·57
Nepheline	—	—	2·23	3·01	—	—	—	5·05	—
Altered nepheline†	—	—	1·76	—	—		—	—	—
Cancrinite	—	—	5·10	—				—	—
Wollastonite ...	0·27	—	0·05	—	—	—	—	0·78	—
Sphene	2·16	—	—	—	—	—	—	4·52	—
Apatite	0·35–0·55	—	—	0·56	—	—	—	—	—
Titano-magnetite ...	2·03	2·15	1·32	2·02	—	—	—	—	—
Pyrochlore	—	9·04	—	—	—	—		—	—
Knopite	0·00	—	—	—	—		—	—	—

* Altering into montmorillonite → natrolite → nepheline.
† Altering into haüyne and nosean.

rocks. As the latter were generated by crystal precipitation at an early epoch of the intrusion, the minerals reflect the very high concentration of CO_2 and comparatively high temperature ruling at that period. The average oxidation level then drops in the case of the nepheline-syenites and still more so in the sövites. This last fact is at first glance somewhat puzzling, but may be explained if we recall that at the time of the 'blowing up' of the diatreme the partial pressure of the CO_2 may have been very high (at least a thousand bars), but that at the same time the temperature was probably rather low. An outstanding exception is the very high oxidation ratio of the pyrochlore, which occurs in a sövite-dike together with phlogopite and aegirine-augite of exceptionally high ratios, 1·96 and 2·44 respectively. Exceptional circumstances must in this case have been responsible for the increased oxidation.

Another interesting feature is the remarkably high oxidation of the

melanite of the ouachitite dike intersecting the sövite of the central cone (Eckermann 4, p. 95). The chemistry of the dike is alnöitic, but the main mineral paragenesis quite different and very simple –melanite, biotite, and calcite. Of the original, probably dolomitic, carbonate nothing remains, but the calcite carries the indication of an earlier dissociation of the magnesite component in the shape of minute vesicles enclosing carbonic acid. The excess of CO_2, in consequence trapped in the dike, may satisfactorily explain the high oxidation ratio of the melanite. Probably the partly greenish biotite is highly oxidized too.

There are good reasons for supposing that in the different run of the oxidation process, viz. the different parts played by the carbonic acid at Archaean limestone contacts and in volcanic vents, may be found one of the answers to the question why in no single instance an alkaline trend of development has been encountered at the thousands of limestone-granite contacts observed in Fennoscandia. Another one may be given by the different behaviour of that most important of hyper-fusibles, the water. Round the 'passive' limestone it is concentrated at low temperature in the pegmatitic rest-solutions, 'provoked into existence'—as I used to express myself in earlier papers—by the premature crystallization of the granite as a result of its enrichment with CaO, while in the case of the active carbonate it is forced by the CO_2 pressure at higher temperature into the surrounding rocks, establishing a 'hydration front' which advances as long as the energy supply from the volcanic vent is maintained. One should therefore expect conspicuous differences in the succession of minerals in the two instances, which is also found to be the case when compiling the parageneses, as has been done in table III.

The silicates of table III have been classified according to atomic structures and their 'dry' (D) or 'hydrous' (H) nature. Dominant minerals are given without brackets; one pair of brackets signifies that the mineral occurs frequently, but in comparatively small amounts, while two pairs denote it as rare. Several minerals have not yet been satisfactorily classified by X-ray studies, as for instance the epidote, where Ito's solution with two linked polyhedra of O and OH around Ca may need confirmation. In the meantime I have adopted Strunz's classification of the mineral. Another doubtful item is the wollastonite, in which case the parawollastonite only has been investigated. The structure of prehnite is actually unknown, but may, according to Strunz, be a complex one. Its classification, together with the idocrase, is in consequence a symbolic one only. Finally, one may challenge the position of the analcime as it contains Si_4O_{12}- and Si_6O_{18}-rings in its three-

dimensional framework. All these minerals are marked in the table by a sign of interrogation.

Table III brings out the dominance of hydrous minerals in the case of the Archaean contact parageneses, especially within the silicates containing separate SiO_4 groups. But also within the silicates of silicon-oxygen chains and framework structures a close attention to the 'brackets' will lead to the same conclusion. Only in the case of the sheet structures, viz. the micas, clays, and chlorites, is the frequency of the minerals about equal.

Unfortunately the compilation of the minerals is in one respect not complete. The occurrence of sulphides includes several more species than is given in the table, as for instance blende, marcasite, and chalcopyrite, but the present author was prevented by unforeseen circumstances from working out their distribution in time for this paper. The same applies to rutile, haematite, and goethite. As all these minerals, however, occur as accessories only, their absence does not distort the validity of the broad view of their parageneses and comparison, which table III is meant to give.

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TABLE III. Mineral parageneses at Alnö, Mansjö, Tennberg, and Pargas.

	$(SiO_4)^{4-}$		$(SiO_4)^{4-}+(Si_2O_7)^{6-}$	$(Si_2O_7)^{6-}$	$(Si_3O_9)^{6-}$	$\infty(SiO_3)^{2-}$	$\infty(Si_4O_{11})^{6-}$	$\infty(Si_2O_4)^{2-}$	∞ n((Si,Al)O_4)		Carbonates: cc calcite, mgt magnesite, cbt chalybite	Sulphides and sulphates	Oxides.	Not classified minerals.
	D	H	H	D	D	D	H	H	D	H				
Alnö parageneses:														
Sövites	(Forsterite)	((Mn-Epidote)) ?	—	—	(Wollastonite) ?	Diopsidic augite (Aeg.-augite)	((Serpentine))	(Meroxene) (Phlogopite) ((Manganophyllite))			cc mgt cbt 100-90 0-10 0	Pyrite (Pyrrhotine) Baryte ((Arsenopyrite))	(Magnetite)	F-apatite, (Knopite) ((Dahllite)), (Dysanalyte) Fluorite, (Pyrochlore) (Perovskite)
Alvikites	(Forsterite) (Andradite)	—	—	((Melilite))	(Wollastonite) ?	augite (Aeg.-augite)		((Meroxene)) (Phlogopite)	(Orthoclase) ((Nepheline))	(Natrolite)	cc mgt cbt 100-84 0-16 0-4	Pyrite (Pyrrhotine)	(Magnetite) (Corundum)	F-apatite, Fluorite (Perovskite), CO_2
Nepheline-syenites	Melanite (Sphene)	—	—	—	—	Aeg.-augite		—	Nepheline Na-orthoclase	Cancrinite (Natrolite)	((cc mgt)) 100-94 0-6	(Pyrite)	((Magnetite))	(F-apatite) (Perovskite)
Nephelinitic dikes	(Melanite)	—	—	—	—	Aegirine Aeg.-augite (Pigeonite)		—	Nepheline Anorthoclase Na-orthoclase	(Analcime) ?	((cc mgt cbt)) 100-92 0-8 0-4 ((Dawsonite))	(Pyrite)	(Magnetite) (Ilmenite)	(F-apatite, Fluorite) (Perovskite)
Vibetoides	—		—	—	—	Aeg.-augite	Barkevikitic-hornblende	Biotite (Lepidomelane)			((cc mgt cbt)) 100 0 0	(Pyrite)	Ti-magnetite	F-apatite
Jacupirangites	Melanite (Sphene)		—	((Melilite))	—	Ti-augite	((Barkevikitic-hornblende))	Lepidomelane			((cc mgt cbt)) 100 0 0	((Pyrite))	Ti-magnetite	F-apatite
Beforsites	(Olivine) (Monticellite) ((Sphene))		—	(Melilite)	—		(Riebeckite) (Serpentine)	(Meroxene) Phlogopite (Anomite)	(Orthoclase) (Na-orthoclase)		cc mgt cbt 40-80 60-5 0-20 (Strontianite)	(Pyrite) (Pyrrhotine) ((Baryte))	(Ti-magnetite) (Ilmenite) (Anatase)	(F-apatite), Fluorite Perovskite, CO_2 ((Chalcedony))
Alnöites and Kimberlites	Monticellite Olivine (Andradite)	—	—	Melilite	—	Augite (Ti-augite)	(Basaltic-hornblende) (Serpentine)	Anomite (Meroxene)		(Analcime) ?	(cc mgt cbt 100-55 0-45 0-4	((Pyrite)) ((Baryte))	(Ti-magnetite) (Chromite)	F-apatite Perovskite
Melanite-Ouachitites	Melanite	—	—	—	—	—	—	Meroxene	—	—	cc mgt cbt 100-90 0-10 0	(Pyrite)	(Ti-magnetite)	F-apatite, (CO_2) (Perovskite)
Syenitic fenites	Sphene (Andradite)	—	—	—	—	Aeg.-augite		Montmorillonite (Biotite)	Perthite (Na-orthoclase)	Natrolite	((cc mgt cbt)) 100 0 0	(Pyrite) ((Baryte))	(Quartz)	((F-apatite))
Nephelinitic fenites	Melanite (Sphene)	—	—	—	Wollastonite ?	Aeg.-augite (Aegirine)	—		Nepheline Na-orthoclase	(Natrolite)	(cc mgt cbt) 100 0 0	((Pyrite)) (Baryte)	((Ti-magnetite)) ((Baddeleyite))	(F-apatite)
Basic fenites	Melanite	—	—	—	—	Aeg.-augite (Ti-augite)		(Biotite)	((Nepheline))	((Natrolite))	(cc mgt cbt) 100-90 0-10 0-2	(Pyrite)	Ti-magnetite	F-apatite
Archaean parageneses:														
Mansjö limestone contact	Sphene Grossular	Chondrodite	Idocrase Prehnite ?	—	Wollastonite ?	Diopside Mansjöite	Pargasite	Phlogopite	Microcline	Scapolite Anorthite	cc mgt cbt 100 0 0	(Pyrite)	Alkali-spinel ((Zircon)) ((Quartz))	(F,Cl)-apatite, Fluorite (Orthite), (scheelite)
Tennberg limestone contact	Grossular (Sphene)	(Chondrodite)	Idocrase	—	Wollastonite ?	Diopside	(Pargasite)	Phlogopite (Pennine)	—	—	cc mgt cbt 100 0 0	—	(Quartz) (Perclase)	(Apatite)
Contact aureole of Tennberg granite	Sphene	Epidote ?	(Prehnite) ?	—	-	Diopsidic-augite	Hastingsite	—	Andesine (Albite)	(Tourmaline)	—	—	Quartz	—
Pargas limestone contact	Sphene Grossular	Chondrodite	Idocrase (Prehnite) ?	-	Wollastonite ?	Diopside	Pargasite (Tremolite) (Pyrallolite)	Phlogopite Clintonite	Microcline Oligoclase to Anorthite	Scapolite (Anorthite) (Tourmaline)	cc mgt cbt 100-50 50-0 0	Pyrite ((Arsenopyrite)) (Pyrrhotine) ((Lollingite)) ((Chalcopyrite))	((Zircon)) (Quartz) Spinel Ilmenite	Apatite, Fluorite (Orthite) Graphite

Angular relations between equivalent planes and distances between equivalent points in symmetrical point groups

By Paul Niggli
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A FUNDAMENTAL problem arising out of the study of symmetrical point groups can be formulated as follows: Let N points in three-dimensional space be connected two and two in every possible way by straight lines: what relations must exist between the lengths of these lines if the points are equivalent members of a symmetrical point group?

The methods of projection used in crystallography (e.g. the stereographic projection) at once show that the points may be considered to be the images of straight lines or planes. The problem formulated above has therefore a direct application to descriptive crystallography and can in this connexion be stated as follows:

A complex of N planes is determined by the points of intersection of the normals with the surface of a unit sphere, i.e. by their *poles*. What now must the angular relations between the planes be if all are equivalent, that is to say, belong to one and the same simple form?

The connecting lines between the points are in this case replaced by the angles between the normals of the planes, and in treating this problem it will be useful to substitute these angles by their characteristic cosine values.

If we proceed from any one plane and determine the angles between its normal and those of the $(N-1)$ other planes, it is obvious that these will only be equivalent to the first if certain quite specific relations exist between the angles (or their cosines). These relations we desire to express in formulae.

If all N planes are equivalent, it is, of course, immaterial which we select as the point of departure. Let the planes be numbered from 1 to N and the cosines of the angles between all possible pairs of planes be written in the form of a square matrix. Every row and every column of the matrix must now contain all the cosine values which differ from one another. When written in the usual way, the matrix possesses symmetrical structure in respect to the chief diagonal which contains the values $\cos 0° = 1$. With this fundamental condition others are associated

which determine the symmetry and the special character of the form constituted by the equivalent planes.

The position of a pole in respect to the elements of symmetry passing through the centre of the sphere determines the position of the remaining poles and therefore also the angles between the planes. Let the position of the first pole be expressed in terms of the usual co-ordinate angles ϕ and ρ. This is shown in fig. 1 for the complex of planes constituting a dihexagonal pyramid. Our problem now consists in expressing the cosines of the angles between plane 1 and the $(N-1)$ other planes in terms of the ϕ- and ρ-values of the plane of departure.

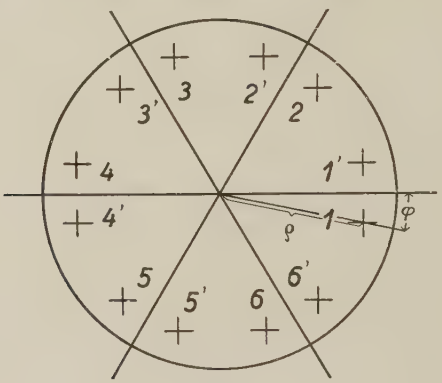

Fig. 1.

In order to obtain the matrix in an easily defined form, it is proposed to use the groupings into cycles commonly employed in the investigation of symmetry. The study of point symmetry leads, as is well known, to the distinction of three principal cases: (1) symmetries with a unique axis (including the orthorhombic, monoclinic, and triclinic symmetries as trivial specializations); (2) the isometric cubic symmetries; (3) the isometric symmetries.

1. *Matrix representation of symmetries with a unique axis.*

In symmetries of this sort we select the highest rotation cycles and proceed to number the poles anti-clockwise from 1 to n, n being the valency of the axis. The unique axis as the rotation axis with the highest valency having thus the valency n, the number of equivalent elements in the derived symmetry groups can at most be $4n = N$. For instance, n planes of symmetry parallel to the unique axis, or n binary axes perpendicular to the same, or a centre of symmetry, or a plane o

symmetry perpendicular to the unique axis may be present. If $N = 4n$, which implies that the group has holohedral character, the total matrix may be resolved into 4×4 submatrices comprising $n \times n$ constituents.

Let the n poles required to augment an n-gonal pyramid to a di-n-gonal one be termed $1' \ldots x' \ldots n'$, the count being taken in the same anticlockwise sense as hitherto (see fig. 1). Further let the mirror images of $1 \ldots x \ldots n$ with respect to planes of symmetry perpendicular to the unique axis be called $(1) \ldots (x) \ldots (n)$ and those of $1' \ldots x' \ldots n'$ bear the numbers $(1') \ldots (x') \ldots (n')$. For the dihexagonal bipyramid, for

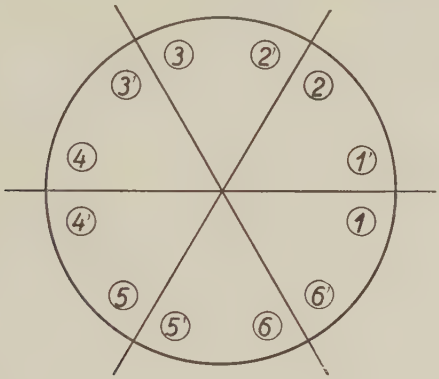

FIG. 2.

instance, fig. 2 with its poles on the lower half of the sphere must now be considered in conjunction with fig. 1. A summary of the possible forms resulting from $n = 6$ can at once be given as follows:

1 2 3 4 5 6 = the hexagonal pyramid or when $\rho = 90°$ the hexagonal prism.

1 2 3 4 5 6 together with 1′ 2′ 3′ 4′ 5′ 6′ = the dihexagonal pyramid or when $\rho = 90°$ the dihexagonal prism.

1 2 3 4 5 6 together with (1) (2) (3) (4) (5) (6) = the hexagonal bipyramid.

1 2 3 4 5 6 together with (1′) (2′) (3′) (4′) (5′) (6′) = the hexagonal trapezohedron.

1 2 3 4 5 6 together with 1′ 2′ 3′ 4′ 5′ 6′ and (1) (2) (3) (4) (5) (6) and (1′) (2′) (3′) (4′) (5′) (6′) = the dihexagonal bipyramid.

If the n of a rotation cycle be even, the cycle can be used to derive the $n/2$-gonal classes of symmetry. We obtain for instance:

1 3 5 = the trigonal pyramid or when $\rho = 90°$ the trigonal prism.

1 3 5 (1) (3) (5) = the trigonal bipyramid.

1 3 5 1′ 3′ 5′ = the ditrigonal pyramid or when $\rho = 90°$ the ditrigonal prism.

1 3 5 1′ 3′ 5′ (1) (3) (5) (1′) (3′) (5′) = the ditrigonal bipyramid.

1 3 5 (2) (4) (6) the rhombohedron.

1 3 5 1′ 3′ 5′ (2) (4) (6) (2′) (4′) (6′) the ditrigonal scalenohedron, etc.

With $\rho = 0$ the formulae will become simpler and lead to forms consisting of one plane (pedion) or two planes (pinacoids) respectively.

In a matrix comprising the cosines appropriate to any given n, all forms pertaining to a symmetry class with a unique axis are, therefore, characterized by the angles between the various planes of the form. This is true whether the class of symmetry is a crystallographically possible one or not. A general representation of such a matrix of cosine values is given in table I *a*.

TABLE I *a*. Symbols of the cosine values occurring in the holohedral classes of symmetry with a unique axis.

	1	2	...	$n-1$	n	1′	2′	...	$(n'-1)$	n'	(1)	(2)	...	$(n-1)$	(n)	(1′)	(2′)	...	$(n'-$
1	1 (α_0)	α_1	...	$\alpha_{\bar{2}}$	$\alpha_{\bar{1}}$	β_0	β_1	...	$\beta_{\bar{2}}$	$\beta_{\bar{1}}$	a_0	a_1	...	$a_{\bar{2}}$	$a_{\bar{1}}$	b_0	b_1	...	$b_{\bar{2}}$
2	$\alpha_{\bar{1}}$	1	...	$\alpha_{\bar{3}}$	$\alpha_{\bar{2}}$	$\beta_{\bar{1}}$	β_0	...	$\beta_{\bar{3}}$	$\beta_{\bar{2}}$	$a_{\bar{1}}$	a_0	...	$a_{\bar{3}}$	$a_{\bar{2}}$	$b_{\bar{1}}$	b_0	...	$b_{\bar{3}}$
⋮			I					II					III					IV	
$n-1$	α_2	α_3	...	1	α_1	β_2	β_3	...	β_0	β_1	a_2	a_3	...	a_0	a_1	b_2	b_3	...	b_0
n	α_1	α_2	...	$\alpha_{\bar{1}}$	1	β_1	β_2	...	$\beta_{\bar{1}}$	β_0	a_1	a_2	...	$a_{\bar{1}}$	a_0	b_1	b_2	...	$b_{\bar{1}}$
1′	β_0	$\beta_{\bar{1}}$	...	β_2	β_1	1	α_1	...	$\alpha_{\bar{2}}$	$\alpha_{\bar{1}}$	b_0	$b_{\bar{1}}$	...	b_2	b_1	a_0	a_1	...	$a_{\bar{2}}$
2′	β_1	β_0	...	β_3	β_2	$\alpha_{\bar{1}}$	1	...	$\alpha_{\bar{3}}$	$\alpha_{\bar{2}}$	b_1	b_0	...	b_3	b_2	$a_{\bar{1}}$	a_0	...	$a_{\bar{3}}$
⋮			II′					I					IV′					III	
$n'-1$	$\beta_{\bar{2}}$	$\beta_{\bar{3}}$	...	β_0	$\beta_{\bar{1}}$	α_2	α_3	...	1	α_1	$b_{\bar{2}}$	$b_{\bar{3}}$	...	b_0	$b_{\bar{1}}$	a_2	a_3	...	a_0
n'	$\beta_{\bar{1}}$	$\beta_{\bar{2}}$	...	β_1	β_0	α_1	α_2	...	$\alpha_{\bar{1}}$	1	$b_{\bar{1}}$	$b_{\bar{2}}$	...	b_1	b_0	a_1	a_2	...	$a_{\bar{1}}$
(1)	a_0	a_1	...	$a_{\bar{2}}$	$a_{\bar{1}}$	b_0	b_1	...	$b_{\bar{2}}$	$b_{\bar{1}}$	1	α_1	...	$\alpha_{\bar{2}}$	$\alpha_{\bar{1}}$	β_0	β_1	...	$\beta_{\bar{2}}$
(2)	$a_{\bar{1}}$	a_0	...	$a_{\bar{3}}$	$a_{\bar{2}}$	$b_{\bar{1}}$	b_0	...	$b_{\bar{3}}$	$b_{\bar{2}}$	$\alpha_{\bar{1}}$	1	...	$\alpha_{\bar{3}}$	$\alpha_{\bar{2}}$	$\beta_{\bar{1}}$	β_0	...	$\beta_{\bar{3}}$
⋮			III					IV					I					II	
$(n-1)$	a_2	a_3	...	a_0	a_1	b_2	b_3	...	b_0	b_1	α_2	α_3	...	1	α_1	β_2	β_3	...	β_0
(n)	a_1	a_2	...	$a_{\bar{1}}$	a_0	b_1	b_2	...	$b_{\bar{1}}$	b_0	α_1	α_2	...	$\alpha_{\bar{1}}$	1	β_1	β_2	...	$\beta_{\bar{1}}$
(1′)	b_0	$b_{\bar{1}}$	...	b_2	b_1	a_0	a_1	...	$a_{\bar{2}}$	$a_{\bar{1}}$	β_0	$\beta_{\bar{1}}$	...	β_2	β_1	1	α_1	...	$\alpha_{\bar{2}}$
(2′)	b_1	b_0	...	b_3	b_2	$a_{\bar{1}}$	a_0	...	$a_{\bar{3}}$	$a_{\bar{2}}$	β_1	β_0	...	β_3	β_2	$\alpha_{\bar{1}}$	1	...	$\alpha_{\bar{3}}$
⋮			IV′					III					II′					I	
$(n'-1)$	$b_{\bar{2}}$	$b_{\bar{3}}$	...	b_0	$b_{\bar{1}}$	a_2	a_3	...	a_0	a_1	$\beta_{\bar{2}}$	$\beta_{\bar{3}}$	...	β_0	$\beta_{\bar{1}}$	α_2	α_3	...	1
(n')	$b_{\bar{1}}$	$b_{\bar{2}}$	...	b_1	b_0	a_1	a_2	...	$a_{\bar{1}}$	a_0	$\beta_{\bar{1}}$	$\beta_{\bar{2}}$	...	β_1	β_0	α_1	α_2	...	$\alpha_{\bar{1}}$

Let the cosines of the angles between the poles 1 and x in the series $1 \ldots x \ldots n$ be symbolized by α_{x-1}. If the angle between the poles 1 and x is greater when measured anti-clockwise, the expression α_{x-1-n} is used in order always to operate with the cosine of the smaller angle. Thus $\alpha_{n-1} = \alpha_{\bar{1}}$, $\alpha_{n-2} = \alpha_{\bar{2}}$, etc.

Similarly, the cosines of the angles between the poles 1 and x' are symbolized by $\beta_{x'\ 1}$ or $\beta_{x'-1\ -n}$, those of the angles between 1 and (x) by α_{x-1} or a_{x-1-n}, and, finally, those of the angles between 1 and (x') by α_{x-1} or b_{x-1-n}.

If n is even, the angles between 1 and $n/2$ or 1 and $n'/2$ or 1 and $(n/2)$ or and $(n'/2)$ separate the positive and negative index values. Assuming all points or planes to be equivalent, every row or column of a submatrix

$$||\alpha_{ik}|| \quad \text{or} \quad ||a_{ik}|| \quad \text{or} \quad ||\beta_{ik}|| \quad \text{or} \quad ||b_{ik}||$$

evidently contains the same number of and at most n different cosine values. Also the relation obtains

$$\alpha_i = \alpha_{\bar{i}} \text{ (e.g. } \alpha_2 = \alpha_{\bar{2}}) \quad \text{and} \quad a_i = a_{\bar{i}} \text{ (e.g. } a_1 = a_{\bar{1}}).$$

The square submatrices I and III which each appear four times in the holohedral general matrix are thus symmetrical in themselves. Therefore when n is even, the subsquares I can by their very nature contain at most $n/2$ different cosine values. These include α_0 representing the value of $\cos 0^\circ = 1 - \cos^2\rho + \sin^2\rho$ and $\alpha_{n/2}$ representing the value of $\cos 2\rho = \cos^2\rho - \sin^2\rho$. If n is odd, the last-named value does not occur and the number of different cosine values is $1+(n-1)/2$.

In the subsquare III the number of different cosine values is the same. However, $a_0 = \cos(\measuredangle 1 \text{ to } (1)) = \cos^2\rho + \sin^2\rho$ and $a_{n/2} = -1$. The latter value does not occur when n is odd. Quite generally

$$\alpha_i = \alpha_{\bar{i}} = \cos^2\rho + \sin^2\rho . \cos \frac{i.360}{n}$$

and

$$a_i = a_{\bar{i}} = -\cos^2\rho + \sin^2\rho . \cos \frac{i.360}{n}.$$

In the submatrices I the sum of all cosine values belonging to one row or column (i.e. $\sum \alpha_i$) is given by $n \cos^2\rho$, for the sum $\cos\{(i.360/n)\}$ of the angles derived from one rotation axis is always zero. Similarly, the sum $\sum a_i$ of any row or column is $-n \cos^2\rho$.

The submatrices or subsquares containing the n_β or n_b values each give rise to two matrices, namely, II and II′ and IV and IV′ respectively, of which the primed ones are conjugated to the non-primed. The submatrices II, II′, and IV, IV′ each contain at most n different cosine values which occur once in each row and column.

$$\beta_0 \text{ is } \cos^2\rho + \sin^2\rho \cos 2\phi$$

and when n is even

$$\beta_{n/2} = \beta_{\bar{n}/2} = \cos^2\rho - \sin^2\rho \cos 2\phi,$$

b_0 is $-\cos^2\rho+\sin^2\rho\cos 2\phi$ and when n is even,

$$b_{n/2} = b_{\overline{n}/2} = -\cos^2\rho-\sin^2\rho\cos 2\phi.$$

β_i no longer equals $\beta_{\bar{i}}$, nor is $b_i - b_{\bar{i}}$. The values of these expressions are now given by

$$\beta_i = \cos^2\rho+\sin^2\rho\cos\left(\frac{i.360}{n}+2\phi\right);$$

$$\beta_{\bar{i}} = \cos^2\rho+\sin^2\rho\cos\left(\frac{i.360}{n}-2\phi\right);$$

$$b_i = -\cos^2\rho+\sin^2\rho\cos\left(\frac{i.360}{n}+2\phi\right);$$

$$b_{\bar{i}} = -\cos^2\rho+\sin^2\rho\cos\left(\frac{i.360}{n}-2\phi\right).$$

It can, however, easily be shown that the following relations still obtain:

Sum of all the cosine values in any row or column of II or II′

$$= n\cos^2\rho.$$

Sum of all the cosine values in any row or column of IV or IV′

$$= -n\cos^2\rho.$$

These conditions and the arrangement of the minor squares show that the general holohedral matrix possesses centrosymmetrical structure. The chief diagonals contain only ones and the trace has the value N. Table I*b* gives a summary of these results.

TABLE I*b*.

General formulae for the cosine values.	Specal case for identity.	Special case applicable only when n is even.
$\alpha_{\pm i} = \cos^2\rho+\sin^2\rho\cos i\frac{2\pi}{n}$	$\alpha_0 = 1$	$\alpha_{n/2} = \cos^2\rho-\sin^2\rho$
$\beta_{\pm i} = \cos^2\rho+\sin^2\rho\cos\left(i\frac{2\pi}{n}\pm 2\phi\right)$	$\beta_0 = \cos^2\rho+\sin^2\rho\cos 2\phi$	$\beta_{n/2} = \cos^2\rho-\sin^2\rho\cos 2\phi$
$a_{\pm i} = -\cos^2\rho+\sin^2\rho\cos i\frac{2\pi}{n}$	$a_0 = -\cos^2\rho+\sin^2\rho$	$a_{n/2} = -1$
$b_{\pm i} = -\cos^2\rho+\sin^2\rho\cos\left(i\frac{2\pi}{n}\pm 2\phi\right)$	$b_0 = -\cos^2\rho+\sin^2\rho\cos 2\phi$	$b_{n/2} = -\cos^2\rho-\sin^2\rho\cos 2\phi$

If the arrangement of the points or planes n is centrosymmetrical, each positive cosine value requires the presence of an equal negative cosine value. When n is even, the corresponding values may be expressed as

$$\cos^2\rho+\sin^2\rho\cos\frac{i.360}{n} \quad \text{and} \quad -\cos^2\rho+\sin^2\rho\cos\frac{i'.360}{n}$$

in which $i' = n/2+i$. We now, however, write $\bar{i}$ instead of i' and $\bar{i} = n/2-\bar{i}$. Thus with $n = 6$ we obtain the value

$$\cos\frac{1.360}{6} = -\cos\frac{(3+1).360}{6} = -\cos\frac{2.360}{6}.$$

Therefore $\alpha_{\bar{2}} = -\alpha_1$.

Let the total number of different cosine values be Z and the number of cosines different in absolute value only (i.e. irrespective of signs) be z. The following relations can now be established in the series.

n divisible by 4. Beside 1, $\bar{1}$, 0, 0 the other values appear twice with positive and twice with negative signs. z is therefore given by

$$\frac{n-4}{4}+2 = \frac{n+4}{4}.$$

For instance, in the case of a 12-fold axis the $\cos\{(i.360)/12\}$ are as follows:

1 0·866 0·5 0 −0·5 −0·866 −1 −0·866

−0·5 0 0·5 0·866.

n only divisible by 2. Beside 1 and $\bar{1}$ every other cosine value appears twice with positive and twice with negative sign. The total number of numerical values $\cos\{(i.360)/n\}$ (irrespective of signs) is

$$z = \frac{n-2}{4}+1 = \frac{n+2}{4}.$$

For the series $\cos\{(i.360)/6\}$ the values are:

1 0·5 −0·5 −1 −0·5 0·5.

n odd. Beside 1 every other cosine value appears twice with the same sign. Although a given positive numerical value no longer leads to the corresponding negative numerical value, the expression $\sum\cos\{(i.360)/n\}$ in which i varies from 0 to $n-1$) remains zero.

As a result of the conditions contained in the above formulae, the entire range of cosine values contained in the matrix consists of functions of ϕ, or of these and 2ϕ. Naturally the following relations obtain:

$$\cos\left(\frac{i.360}{n}+2\phi\right) = \cos\frac{i.360}{n}\cos 2\phi - \sin\frac{i.360}{n}\sin 2\phi,$$

$$\cos\left(\frac{i.360}{n}-2\phi\right) = \cos\frac{i.360}{n}\cos 2\phi + \sin\frac{i.360}{n}\sin 2\phi.$$

In terms of the theory of matrices the results obtained in connexion with forms deriving from symmetry with a unique axis may be summarized as follows:

Square N-rowed matrix for holohedral classes with a unique di-n-gonal axis.

$$||g_{ik}||_N = \left\| \begin{matrix} \text{I} & \text{II} & \text{III} & \text{IV} \\ \text{II}' & \text{I} & \text{IV}' & \text{III} \\ \text{III} & \text{IV} & \text{I} & \text{II} \\ \text{IV}' & \text{III} & \text{II}' & \text{I} \end{matrix} \right\| \quad N = 4n$$

with square n-rowed submatrices as constituents:

$$\begin{aligned} \text{I} &= \sin^2\rho||a_{ik}||_n + \cos^2\rho||c_{ik}||_n \\ \text{II} &= \sin^2\rho||b_{ik}||_n + \cos^2\rho||c_{ik}||_n \\ \text{II}' &= \sin^2\rho||b_{ki}||_n + \cos^2\rho||c_{ik}||_n \\ \text{III} &= \sin^2\rho||b_{ik}||_n - \cos^2\rho||c_{ik}||_n \\ \text{IV} &= \sin^2\rho||b_{ik}||_n - \cos^2\rho||c_{ik}||_n \\ \text{IV}' &= \sin^2\rho||b_{ki}||_n - \cos^2\rho||c_{ik}||_n \end{aligned}$$

$$a_{ik} = \cos\left[(k-i)\,\frac{2\pi}{n}\right]; \; c_{ik} = 1$$

$$b_{ik} = \cos\left[(k-i)\frac{2\pi}{n} \pm 2\phi\right] \quad \text{with } + \text{ for } k \geqslant i,$$

$||b_{ki}||_n$ is the transposed form of $||b_{ik}||_n$. Therefore II′ and IV′ are the transposed forms of II and IV.

Because $g_{ii} = 1$, the trace of $||g_{ik}||_N = N$.

The necessary and sufficient conditions have now been given which must be fulfilled by the cosine values of the angles between any plane and the other equivalent ones if the general matrix figure 1 is to possess the symmetry corresponding to forms with a unique axis. No distinction has been made between crystallographic and non-crystallographic forms. The results may briefly be stated as follows:

Equipoints as in the di-n-gonal bipyramid. The matrix contains the I-, II-, II′-, III-, IV-, IV′-squares. The sum of the constituents in each row or column is zero.

Equipoints as in the n-gonal bipyramid. The matrix contains two I- and two III-squares. The sum of the constituents in each row or column is zero.

Equipoints as in the n-gonal trapezohedron. The matrix contains two I-, one IV-, and one IV′-square. The sum of the constituents in each row or column is zero.

Equipoints as in the di-n-gonal pyramid. The matrix contains I-, II-, II′-, I-squares. The sum of the constituents in each row or column is $2n\cos^2\rho$. For the di-n-gonal prism $\cos\rho = 0$ and the sum of the constituents in each row or column again becomes zero.

Equipoints as in the n-gonal pyramid. The matrix contains only I. The number of different values is $n/2$ or $(n+1)/2$. The sum of the constituents in each row or column is $n\cos^2\rho$ and zero for the n-gonal prism. For matrices corresponding to scalenohedra and streptohedra (e.g. rhombohedra) see page 316.

T. Liebisch[1] considered the angles $1/1'$ and also $1/n'$ and $1/(1)$ as fundamentally important for di-n-gonal di-pyramids. They can be deduced[2] from our general formulae for any given n and as functions of ϕ and ρ. The same applies to all fundamental angles of forms deriving from symmetry with a unique axis. It is equally easy to determine the distances between equivalent points arranged around a central point. This is an important problem in the investigation of co-ordination patterns within crystal structures. For this purpose the distance of a point from the chief point of symmetry is taken as 1. If the lines between equivalent points and the chief point of symmetry comprise the angle ϵ, the square of the distance between the points is then $d_\epsilon^2 = 2-2\cos\epsilon$. For $\cos\epsilon$ we can substitute the α_i–, β_i–, a_i–, b_i–values. If in a general matrix containing the d^2–values, the sum of the cosines be zero (when α_i, β_i, a_i, b_i are the constituents of the rows and columns), then the matrix of the d^2-values must consist of numbers whose sum in each row or column of the subsquares is $2n$. This is true for all non-polar forms. For groups corresponding to the di-n-gonal di-pyramid the sums of the rows or columns containing d^2–values is $8n$.

[1] Theodor Liebisch, Geometrische Krystallographie. Leipzig, 1881, p. 223.

[2] The following formulae are convenient in calculations connected with forms deriving from symmetry with a unique axis.

$$\alpha_1-\cos^2\rho = \sin^2\rho\cos\frac{2\pi}{n}; \qquad \beta_0-\cos^2\rho = \sin^2\rho\cos 2\phi$$

$$(1+a_0)\cos 2\phi = 2\beta_0+a_0-1 = 2b_0-a_0+1$$

$$(1+a_0)\cos\frac{2\pi}{n} = 2\alpha_1+a_0-1 = 2a_1-a_0+1$$

$$(1+a_0)\cos\left(\frac{2\pi}{n}-2\phi\right) = 2\beta_{\bar{1}}+a_0-1 = 2b_{\bar{1}}-a_0+1$$

$$(1+a_0)\cos\left(\frac{2\pi}{n}+2\phi\right) = 2\beta_1+a_0-1 = 2b_1-a_0+1$$

It therefore follows that:

$$a_1 = \alpha_1+a_0-1; \qquad b_{\bar{1}} = \beta_{\bar{1}}+a_0-1; \qquad b_0 = \beta_0+a_0-1, \text{ etc.}$$

The ϕ angles and $\cos\frac{2\pi}{n}$ can each be calculated from two angular values. As

$$\cos\left(\frac{2\pi}{n}-2\phi\right)+\cos\left(\frac{2\pi}{n}+2\phi\right) = 2\cos\frac{2\pi}{n}\cos 2\phi,$$

further equations can be derived.

The characteristic values for $n = 6$ in both representations are given in the top rows of tables II and III.

TABLE II

Cosine values of the angles for $n = 6$.

I

	1	2	3
1	1	$\cos^2\rho+\frac{1}{2}\sin^2\rho$	$\cos^2\rho-\frac{1}{2}\sin^2\rho$
	4	5	6
1	$\cos^2\rho-\sin^2\rho$	$\cos^2\rho-\frac{1}{2}\sin^2\rho$	$\cos^2\rho+\frac{1}{2}\sin^2\rho$

II

	1′	2′	3′
1	$\cos^2\rho+\sin^2\rho\cos 2\phi$	$\cos^2\rho+\sin^2\rho\cos(60+2\phi)$	$\cos^2\rho+\sin^2\rho\cos(120+2\phi)$
	4′	5′	6′
1	$\cos^2\rho-\sin^2\rho\cos 2\phi$	$\cos^2\rho+\sin^2\rho\cos(120-2\phi)$	$\cos^2\rho+\sin^2\rho\cos(60-2\phi)$

III

	(1)	(2)	(3)
1	$\sin^2\rho-\cos^2\rho$	$-\cos^2\rho+\frac{1}{2}\sin^2\rho$	$-\cos^2\rho-\frac{1}{2}\sin^2\rho$
	(4)	(5)	(6)
1	-1	$-\cos^2\rho-\frac{1}{2}\sin^2\rho$	$-\cos^2\rho+\frac{1}{2}\sin^2\rho$

IV

	(1′)	(2′)	(3′)
1	$-\cos^2\rho+\sin^2\rho\cos 2\phi$	$-\cos^2\rho+\sin^2\rho\cos(60+2\phi)$	$-\cos^2\rho+\sin^2\rho\cos(120+2\phi)$
	(4′)	(5′)	(6′)
1	$-\cos^2\rho-\sin^2\rho\cos 2\phi$	$-\cos^2\rho+\sin^2\rho\cos(120-2\phi)$	$-\cos^2\rho+\sin^2\rho\cos(60-2\phi)$

TABLE III

d^2-values for $n = 6$ (squares of the distances of equivalent points) on sphere with unit radius.

I

	1	2	3	4	5	6
1	0	$\sin^2\rho$	$3\sin^2\rho$	$4\sin^2\rho$	$3\sin^2\rho$	$\sin^2\rho$

II

	1′	2′	3′
1	$2\sin^2\rho(1-\cos 2\phi)$	$2\sin^2\rho[1-\cos(60+2\phi)]$	$2\sin^2\rho[1-\cos(120+2\phi)]$
	4′	5′	6′
1	$2\sin^2\rho(1+\cos 2\phi)$	$2\sin^2\rho[1-\cos(120-2\phi)]$	$2\sin^2\rho[1-\cos(60-2\phi)]$

III

	(1)	(2)	(3)	(4)	(5)	(6)
1	$4\cos^2\rho$	$1+3\cos^2\rho$	$3+\cos^2\rho$	4	$3+\cos^2\rho$	$1+3\cos^2\rho$

IV

	(1′)	(2′)	(3′)
1	$4-2\sin^2\rho(1+\cos 2\phi)$	$4-2\sin^2\rho[1+\cos(60+2\phi)]$	$4-2\sin^2\rho[1+\cos(120+2\phi)]$
	(4′)	(5′)	(6′)
1	$4-2\sin^2\rho(1-\cos 2\phi)$	$4-2\sin^2\rho[1+\cos(120-2\phi)]$	$4-2\sin^2\rho[1+\cos(60-2\phi)]$

In the case of $n = 6$, simpler expressions can be obtained by making use of the relations

$$\cos(120+2\phi) = -\cos(60-2\phi); \qquad \cos(60+2\phi) = -\cos(120-2\phi).$$

Also, of course, $\cos^2\rho$ can be recalculated in terms of $\sin^2\rho$ and vice versa.

2. *Matrix representation for isometric symmetry*

Beside the point symmetries characterized by the matrix table I *a*, the following additional equivalent point symmetries now occur:

in cubic symmetry: $N = 4, 6, 8, 12, 24, 48$

in icosahedral symmetry: $N = 12, 20, 30, 60, 120.$

The special forms of the matrix can be deduced for these cases also, but here it is not proposed to go beyond a general discussion of the forms deriving from cubic symmetry.

In the case of the cubic 48-point group we restrict ourselves to giving the cosine values of the top row of the complete matrix out of which everything else follows. The crystallographer will easily follow the sequence used here if the indices of the planes are states whose angles with *hkl* correspond to the given cosines (table IV *a*). However, the

TABLE IV *a*

Top row of the subsquares I–IV for cubic 48-point group

Cosine of the angle included between hkl and:													Number of different z values
I	$\bar{h}kl$	$k\bar{l}h$	lhk	$h\bar{k}\bar{l}$	$k\bar{l}\bar{h}$	$l\bar{h}\bar{k}$	$\bar{h}\bar{k}\bar{l}$	$\bar{k}l\bar{h}$	$\bar{l}h\bar{k}$	$\bar{h}\bar{k}l$	$\bar{k}\bar{l}h$	$\bar{l}\bar{h}k$	
Cosine symbol	A_0	B_0	B_0	A_1	B_3	B_2	A_2	B_1	B_3	A_3	B_2	B_1	8
II	$\bar{h}\bar{l}\bar{k}$	$\bar{l}\bar{k}\bar{h}$	$\bar{k}\bar{h}\bar{l}$	$\bar{h}lk$	$\bar{l}kh$	$\bar{k}hl$	$h\bar{l}k$	$l\bar{k}h$	$k\bar{h}l$	$hl\bar{k}$	$lk\bar{h}$	$kh\bar{l}$	
Cosine symbol	C_1	C_2	C_3	D_1	E_2	E_3	E_1	D_2	E_3	E_1	E_2	D_3	9
III	$\bar{h}\bar{k}\bar{l}$	$\bar{k}\bar{l}\bar{h}$	$\bar{l}\bar{h}\bar{k}$	$\bar{h}kl$	$\bar{k}lh$	$\bar{l}hk$	$h\bar{k}l$	$k\bar{l}h$	$l\bar{h}k$	$hk\bar{l}$	$kl\bar{h}$	$lh\bar{k}$	
Cosine symbol	$-A_0$	$-B_0$	$-B_0$	$-A_1$	$-B_3$	$-B_2$	$-A_2$	$-B_1$	$-B_3$	$-A_3$	$-B_2$	$-B_1$	8
IV	hlk	lkh	khl	$h\bar{l}\bar{k}$	$l\bar{k}\bar{h}$	$k\bar{h}\bar{l}$	$\bar{h}l\bar{k}$	$\bar{l}k\bar{h}$	$\bar{k}h\bar{l}$	$\bar{h}\bar{l}k$	$\bar{l}\bar{k}h$	$\bar{k}\bar{h}l$	
Cosine symbol	$-C_1$	$-C_2$	$-C_3$	$-D_1$	$-E_2$	$-E_3$	$-E_1$	$-D_2$	$-E_3$	$-E_1$	$-E_2$	$-D_3$	9

rules apply quite irrespectively of the rationality of the indices. I contains the tetartohedral equipoints which together with II produce the enantiomorphic, with III the paramorphic, and with IV the hemimorphic classes of symmetry. I to IV are required for cubic holohedral symmetry. Where the same numerical values with negative signs occur in different submatrices, the same letter preceded by a negative sign has been used for the cosine. It is apparent that the 48-point form possesses 17

different values, each appearing positive and negative. Thus there are 34 angular values in all. The matrix of the cubic holohedral 48-plane form (or point group) contains as submatrices all the matrices of the subgroups contained in the group and belonging to the cubic hyposyngony. The ϕ- and ρ- values of the plane of departure are, of course, those corresponding to the cubic setting. The composition of the top row in the matrix in each individual case can be taken from table IV *b* in which N, Z, and z of the general form or point group are given.

TABLE IV *b*. Values for the subgroups of O_h

		N	Z	z
O_h	I II III IV	48	34	17
O	I II	24	17	17
T_d	I IV	24	17	17
T_h	I III	24	16	8
T	I	12	8	8
D_{4h}	$\pm A_0\ A_1\ A_2\ A_3\ C_3\ D_3\ E_3$	16	14	7
D_4	$+A_0\ A_1\ A_2\ A_3\ C_3\ D_3\ E_3$	8	7	7
C_{4h}	$\pm A_0\ A_3\ E_3$	8	6	3
C_{4v}	$+A_0\ A_3\ E_3 - A_1\ A_2\ C_3\ D_3$	8	7	7
D_{2d}	$+A_0\ A_1\ A_2\ A_3 - C_3\ D_3\ E_3$	8	7	7
C_4	$+A_0\ A_3\ E_3$	4	3	3
S_4	$+A_0\ A_3 - E_3$	4	3	3
D_{2h}	$\pm A_0\ A_1\ A_2\ A_3$	8	8	4
D_2	$+A_0\ A_1\ A_2\ A_3$	4	4	4
C_{2v}	$+A_0\ A_3 - A_1\ A_2$	4	4	4
C_{2h}	$\pm A_0\ A_2$	4	4	2
C_2	$+A_0\ A_2$	2	2	2
C_s	$+A_0 - A_2$	2	2	2
C_i	$\pm A_0$	2	2	1
C_1	$+A_0$	1	1	1
D_{3d}	$\pm A_0\ B_0\ C_1\ C_2\ C_3$	12	10	5
D_3	$+A_0\ B_0\ C_1\ C_2\ C_3$	6	5	5
C_{3v}	$+A_0\ B_0 - C_1\ C_2\ C_3$	6	5	5
C_{3i}	$\pm A_0\ B_0$	6	4	2
C_3	$+A_0\ B_0$	3	2	2

The composition of the cosine values symbolized by A_i, B_i, C_i, D_i, E_i is given in table V which consists of four parts. Of these section (*a*) contains a number of computation values which can usefully be derived at the outset of and used during a calculation. Section (*b*) then shows in what manner the 17 cosine values derive from these preliminary ones. The formulae are independent of the law of rationality, but section (*c*) of the table shows the connexions between h, k, and l and the product of two indices on the one hand, and the ϕ-, ρ-values on the other in cases where the law is applicable. In substituting for other planes due care must be given to the signs and sequences of the indices.

The cosines of the angles between (hkl) and the other equivalent rational planes can, as shown by section (c) of table V, always be written in the form $N/(h^2+k^2+l^2)$ in which N can assume the various values given in section (d) of table V.

TABLE V. (Explaining Table IV)

(a) Computation values

$p = \cos^2\rho$	$r = \sin^2\rho \sin^2\phi$	$t = \sin^2\rho \sin 2\phi$	$v = \sin 2\rho \sin \phi$
$q = \sin^2\rho \cos^2\phi$	$s = \sin^2\rho \cos 2\phi$	$u = \sin 2\rho \cos \phi$	$w = \cos 2\rho = \cos^2\rho - \sin^2\rho$

(b) Formation of the cosine values

$A_0 = 1$	$B_0 = \frac{1}{2}(t+u+v)$	$C_1 = -r-u$	$D_3 = -p+t$
$A_1 = -p-s$	$B_1 = \frac{1}{2}(-t+u-v)$	$C_2 = -q-v$	$E_1 = r$
$A_2 = -p+s$	$B_2 = \frac{1}{2}(-t-u+v)$	$C_3 = -p-t$	$E_2 = q$
$A_3 = w$	$B_3 = \frac{1}{2}(t-u-v)$	$D_1 = -r+u$	$E_3 = p$
		$D_2 = -q+v$	

(c) Indices expressed in ρ and ϕ

$h^2 = \sin^2\rho \sin^2\phi\ (h^2+k^2+l^2)$	$kl = \frac{1}{2} \sin 2\rho \cos \phi\ (h^2+k^2+l^2)$
$k^2 = \sin^2\rho \cos^2\phi\ (h^2+k^2+l^2)$	$lh = \frac{1}{2} \sin 2\rho \sin \phi\ (h^2+k^2+l^2)$
$l^2 = \cos^2\rho\ (h^2+k^2+l^2)$	$hk = \frac{1}{2} \sin^2\rho \sin 2\phi\ (h^2+k^2+l^2)$

(d) Calculations of the cosine values for planes with rational indices. Value of

N in $\dfrac{N}{h^2+k^2+l^2}$

$N(A_0) = h^2+k^2+l^2$	$N(B_0) = kl+lh+hk$*	$N(C_1) = -h^2-2kl$	$N(D_3) = -l^2+2hk$
$N(A_1) = h^2-k^2-l^2$	$N(B_1) = kl-lh-hk$*	$N(C_2) = -k^2-2lh$	$N(E_1) = h^2$*
$N(A_2) = -h^2+k^2-l^2$	$N(B_2) = -kl-lh-hk$*	$N(C_3) = -l^2-2hk$	$N(E_2) = k^2$*
$N(A_3) = -h^2-k^2+l^2$	$N(B_3) = -kl-lh+hk$*	$N(D_1) = -h^2+2kl$	$N(E_3) = l^2$*
		$N(D_2) = -k^2+2lh$	

* Can be formed in two different ways.

For the transitional and special forms of the cubic system new conditions arise. They appear whenever ρ or ϕ or both assume special values. Table VI contains all the necessary data. Of course the matrices corresponding to cases with $N < 48$ (e.g. 6, 12, 4, 8, 24) are correspondingly smaller. The complete matrix representation is only required for the hexahedral, tetrahedral, octahedral, and rhombic-dodecahedral point groups in which the angular values are uniquely determined. Tables VII, VIII, and IX give these matrices in the order selected for the 48-point group.

A quite similar treatment can be devoted to the icosahedral group, but the comparative unimportance of the 20-, 30-, 60-, and 120-point groups does not warrant their discussion in this paper.

The regular pentagonal dodecahedron of I and I_h which can also appear as a non-crystallographical form in T and T_h, has as ρ-value 90° and as ϕ-values 31° 43′ or 180° −31° 43′. Five neighbouring planes form angles of 63° 26′ with each plane of the regular pentagonal dodecahedron. As

$$\cos 2\phi = \tfrac{1}{2} \sin 2\phi,\ A_1 = B_1 = B_2 = -0{\cdot}4473$$

and $$A_2 = B_0 = B_3 = 0{\cdot}4473 \quad \text{(see table VI, col. 4).}$$

TABLE VI. Special values for transitional and special forms in the cubic system.

$N = 6$ hexahedral	$N = 12$ rhombic-dodecahedral	$N = 4$ tetrahedral $N = 8$ octahedral	$N = 12$ pentagonal dodecahedral $N = 24$ tetrakishexahedral	$N = 12$ {deltoiddodecahedral, triakistetrahedral} $N = 24$ {triakisoctahedral, deltoidicositetrahedral}
$\rho = 0, \phi = 0$	$\rho = \pi/4, \phi = 0$	$\rho = 54° 44' 8'', \phi = \pi/4$	$\rho = \pi/2$, ϕ any value	ρ any value, $\phi = \pi/4$
$q = r = s = t = u = v = 0$ $p = w = 1$	$r = t = v = w = 0$ $p = q = s = \frac{1}{2}$ $u = 1$	$s = 0$ $p = q = r = \frac{1}{3}$ $t = u = v = \frac{2}{3}$ $w = -\frac{1}{3}$	$p = u = v = 0$ $w = -1$ $q = \cos^2\phi$ $r = \sin^2\phi$ $s = \cos 2\phi$ $t = \sin 2\phi$	$s = 0$ $p = \cos^2\rho$ $t = \sin^2\rho$ $q = r = \frac{1}{2}\sin^2\rho$ $w = \cos 2\rho$ $u = v = \frac{1}{2}\sqrt{2}\sin 2\rho$
$B_0 = B_1 = B_2 = B_3 = C_1 = C_2 = D_1 = D_2 = E_1 = E_2 = 0$ $A_0 = A_1 = A_2 = A_3 = 1$ $C_3 = D_3 = E_3 = -1$	$A_2 = A_3 = E_1 = 0$ $B_0 = B_1 = E_2 = E_3 = \frac{1}{2}$ $B_2 = B_3 = C_2 = C_3 = D_2 = D_3 = -\frac{1}{2}$ $A_0 = D_1 = 1$ $A_1 = C_1 = -1$	$D_1 = D_2 = D_3 = E_1 = E_2 = E_3 = \frac{1}{3}$ $A_1 = A_2 = A_3 = B_1 = B_2 = B_3 = -\frac{1}{3}$ $A_0 = B_0 = 1$ $C_1 = C_2 = C_3 = -1$	$E_3 = 0$ $A_0 = 1$ $A_3 = -1$ $E_2 = \cos^2\phi$ $C_2 = D_2 = -\cos^2\phi$ $E_1 = \sin^2\phi$ $C_1 = D_1 = -\sin^2\phi$ $A_2 = \cos 2\phi$ $A_1 = -\cos 2\phi$ $D_3 = \sin 2\phi$ $C_3 = -\sin 2\phi$ $B_0 = B_3 = \frac{1}{2}\sin 2\phi$ $B_1 = B_2 = -\frac{1}{2}\sin 2\phi$	$A_0 = 1$ $C_3 = -1$ $E_3 = \cos^2\rho$ $A_1 = A_2 = -\cos^2\rho$ $E_1 = E_2 = \frac{1}{2}\sin^2\rho$ $B_1 = B_2 = -\frac{1}{2}\sin^2\rho$ $A_3 = \cos 2\rho = \cos^2\rho - \sin^2\rho$ $D_3 = -\cos 2\rho = \sin^2\rho - \cos^2\rho$ $B_0 = \frac{1}{2}\sin^2\rho + \frac{1}{2}\sqrt{2}\sin 2\rho$ $C_1 = C_2 = -\frac{1}{2}\sin^2\rho - \frac{1}{2}\sqrt{2}\sin 2\rho$ $B_3 = \frac{1}{2}\sin^2\rho - \frac{1}{2}\sqrt{2}\sin 2\rho$ $D_1 = D_2 = -\frac{1}{2}\sin^2\rho + \frac{1}{2}\sqrt{2}\sin 2\rho$
$Z = 3$ $z = 2$ 5 or 14 equations	$Z = 5$ $z = 3$ 3 or 12 equations	$N = 4$: $Z = 2$, $z = 2$ $N = 8$: $Z = 4$, $z = 2$ 6 or 13 equations	$N = 12$: $Z = 6$, $z = 3$ $N = 24$: $Z = 13$, $z = 7$ 2 or 4 equations	$N = 12$: $Z = 6$, $z = 6$ $N = 24$: $Z = 12$, $z = 6$ 2 or 5 equations

TABLE VII. Hexahedral matrix. (Cosine values.)

	001	010	100	00$\bar{1}$	0$\bar{1}$0	$\bar{1}$00
	1	2	3	4	5	6
1	1	0	0	−1	0	0
2	0	1	0	0	−1	0
3	0	0	1	0	0	−1
4	−1	0	0	1	0	0
5	0	−1	0	0	1	0
6	0	0	−1	0	0	1

TABLE VIII. Tetrahedral and octahedral matrix. (Cosine values.)

		I				II				
		111	1$\bar{1}$1	$\bar{1}$1$\bar{1}$	$\bar{1}\bar{1}$1	$\bar{1}\bar{1}\bar{1}$	$\bar{1}$11	1$\bar{1}$1	11$\bar{1}$	
		1	2	3	4	5	6	7	8	
I	1	1	$-\frac{1}{3}$	$-\frac{1}{3}$	$-\frac{1}{3}$	−1	$\frac{1}{3}$	$\frac{1}{3}$	$\frac{1}{3}$	II
	2	$-\frac{1}{3}$	1	$-\frac{1}{3}$	$-\frac{1}{3}$	$\frac{1}{3}$	−1	$\frac{1}{3}$	$\frac{1}{3}$	
	3	$-\frac{1}{3}$	$-\frac{1}{3}$	1	$-\frac{1}{3}$	$\frac{1}{3}$	$\frac{1}{3}$	1	$\frac{1}{3}$	
	4	$-\frac{1}{3}$	$-\frac{1}{3}$	$-\frac{1}{3}$	1	$\frac{1}{3}$	$\frac{1}{3}$	$\frac{1}{3}$	−1	
II	5	−1	$\frac{1}{3}$	$\frac{1}{3}$	$\frac{1}{3}$	1	$-\frac{1}{3}$	$-\frac{1}{3}$	$-\frac{1}{3}$	I
	6	$\frac{1}{3}$	−1	$\frac{1}{3}$	$\frac{1}{3}$	$-\frac{1}{3}$	1	$-\frac{1}{3}$	$-\frac{1}{3}$	
	7	$\frac{1}{3}$	$\frac{1}{3}$	−1	$\frac{1}{3}$	$-\frac{1}{3}$	$-\frac{1}{3}$	1	$-\frac{1}{3}$	
	8	$\frac{1}{3}$	$\frac{1}{3}$	$\frac{1}{3}$	−1	$-\frac{1}{3}$	$-\frac{1}{3}$	$-\frac{1}{3}$	1	
		I				II				

I = Tetrahedron. I+II = Octahedron

TABLE IX. Rhombic dodecahedral matrix. (Cosine values.)

	011	110	101	0$\bar{1}\bar{1}$	1$\bar{1}$0	10$\bar{1}$	01$\bar{1}$	$\bar{1}$10	$\bar{1}$0$\bar{1}$	0$\bar{1}$1	$\bar{1}\bar{1}$0	$\bar{1}$01
	1	2	3	4	5	6	7	8	9	10	11	12
1	1	$\frac{1}{2}$	$\frac{1}{2}$	−1	$-\frac{1}{2}$	$-\frac{1}{2}$	0	$\frac{1}{2}$	$-\frac{1}{2}$	0	$-\frac{1}{2}$	$\frac{1}{2}$
2	$\frac{1}{2}$	1	$\frac{1}{2}$	$-\frac{1}{2}$	0	$\frac{1}{2}$	$\frac{1}{2}$	0	$-\frac{1}{2}$	$-\frac{1}{2}$	−1	$-\frac{1}{2}$
3	$\frac{1}{2}$	$\frac{1}{2}$	1	$-\frac{1}{2}$	$\frac{1}{2}$	0	$-\frac{1}{2}$	$-\frac{1}{2}$	−1	$\frac{1}{2}$	$-\frac{1}{2}$	0
4	−1	$-\frac{1}{2}$	$-\frac{1}{2}$	1	$\frac{1}{2}$	$\frac{1}{2}$	0	$\frac{1}{2}$	$\frac{1}{2}$	0	$\frac{1}{2}$	$-\frac{1}{2}$
5	$-\frac{1}{2}$	0	$\frac{1}{2}$	$\frac{1}{2}$	1	$\frac{1}{2}$	$-\frac{1}{2}$	-1	$-\frac{1}{2}$	$\frac{1}{2}$	0	$-\frac{1}{2}$
6	$-\frac{1}{2}$	$\frac{1}{2}$	0	$\frac{1}{2}$	$\frac{1}{2}$	1	$\frac{1}{2}$	$-\frac{1}{2}$	0	$-\frac{1}{2}$	$-\frac{1}{2}$	−1
7	0	$\frac{1}{2}$	$-\frac{1}{2}$	0	$-\frac{1}{2}$	$\frac{1}{2}$	1	$\frac{1}{2}$	$\frac{1}{2}$	−1	$-\frac{1}{2}$	$-\frac{1}{2}$
8	$\frac{1}{2}$	0	$-\frac{1}{2}$	$-\frac{1}{2}$	−1	$-\frac{1}{2}$	$\frac{1}{2}$	1	$\frac{1}{2}$	$-\frac{1}{2}$	0	$\frac{1}{2}$
9	$-\frac{1}{2}$	$-\frac{1}{2}$	−1	$\frac{1}{2}$	$-\frac{1}{2}$	0	$\frac{1}{2}$	$\frac{1}{2}$	1	$-\frac{1}{2}$	$\frac{1}{2}$	0
10	0	$-\frac{1}{2}$	$\frac{1}{2}$	0	$\frac{1}{2}$	$-\frac{1}{2}$	−1	$-\frac{1}{2}$	$-\frac{1}{2}$	1	$\frac{1}{2}$	$\frac{1}{2}$
11	$-\frac{1}{2}$	−1	$-\frac{1}{2}$	$\frac{1}{2}$	0	$-\frac{1}{2}$	$-\frac{1}{2}$	0	$\frac{1}{2}$	$\frac{1}{2}$	1	$\frac{1}{2}$
12	$\frac{1}{2}$	$-\frac{1}{2}$	0	$-\frac{1}{2}$	$-\frac{1}{2}$	−1	$-\frac{1}{2}$	$\frac{1}{2}$	0	$\frac{1}{2}$	$\frac{1}{2}$	1

There are in all only four different angles and the top line of the matrix in the usual arrangement therefore reads as follows:

A_0	B_0	B_0	A_1	B_3	B_2	A_2	B_1	B_3
1	0·4473	0·4473	−0·4473	0·4473	−0·4473	0·4473	−0·4473	0·4473

A_3	B_2	B_1
−1	−0·4473	−0·4473

$Z = 4$, $z = 2$. The number of equations governing the conditions is four or twelve.

We thus obtain an exact formulation of the laws to be obeyed by a normalized sequence of numbers in a square matrix if the matrix is to be an image of the properties of an equivalent complex within a symmetrical point group. This representation in matrix form is analogous to those called 'vector sets' and 'vector set matrices' by D. M. Wrinch[1] and M. J. Buerger[2] respectively. However, the matrices employed here are restricted to angular values or distances, i.e. to scalar quantities. The application of these methods to the symmetry of vector set matrices of symmetrical point groups presents no difficulties and would elaborate the remarks made by Buerger on this subject.

[1] D. M. Wrinch, Phil. Mag., 1939, vol. 27, p. 98.
[2] M. J. Buerger, Acta Cryst., Cambridge, 1950, vol. 3, p. 87.

Nouvel essai de classification des chlorites

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LES chlorites peuvent être définis d'après G. Tschermak (1), puis A. Lacroix (2), comme des silicates hydratés d'Al, de Mg, et de Fe, de couleur généralement verte, possédant un clivage facile suivant 001), les lames de clivages étant flexibles, sans être élastiques, comme celles du mica. Dans un travail antérieur, l'un de nous (3) avait tenté d'établir une classification de ces minéraux, en se basant directement sur les données de l'analyse chimique, sans faire intervenir d'idée théorique sur leur constitution, comme l'avait fait G. Tschermak et d'autres auteurs après lui. Peu de temps après, un certain nombre de recherches, effectuées à l'aide de rayons X, ont permis d'élucider les caractères essentiels de la structure de ces phyllites.[1] On peut donc raisonnablement en tenter une nouvelle classification chimique tenant compte du schéma structural établi actuellement. C'est ce que nous nous proposons de faire dans ce mémoire, après avoir exposé quelques remarques sur des travaux récents.

Structure des chlorites.

En 1930 Ch. Mauguin (4) a établi, à la suite d'une étude à l'aide des rayons X, que le motif cristallin des chlorites était constitué par un feuillet d'une épaisseur de 14 Å., formé par les translations d'un réseau plan, dont la maille de forme losangique a pour dimensions: $a = 5{\cdot}32$ Å. et $b = 9{\cdot}21$ Å. A peu près à la même époque, Linus Pauling (5) publiait son mémoire général sur la structure des chlorites, dans lequel il précisait que les chlorites sont constitués par la juxtaposition d'un feuillet mica et d'un feuillet brucitique. Cette manière de voir a été confirmée par R. C. McMurchy (6), qui a vérifié les assertions de Pauling, les données numériques de Ch. Mauguin, et de plus a décrit les différents modes d'empilement des feuillets à 14 Å., constituant le minéral. Cette étude a été reprise par d'autres auteurs qui se sont efforcés de préciser les détails de la structure de diverses chlorites, et l'examen des travaux de G. W. Brindley et S. Ali (7), W. von Engelhardt (8) et J. Garrido (9) fait ressortir la variété des assemblages rencontrés.

[1] [A general term used by some French authors for the scaly minerals, micas, chlorites, and clays (J. de Lapparent, Leçons de pétrographie, Paris, 1923, p. 255), and more recently applied to minerals with a layered crystal-structure (L. J. Spencer, 14th list of new mineral names, Min. Mag., 1931, vol. 24, p. 621).]

Tous ces travaux ont, cependant, vérifié dans leurs grandes lignes la structure des chlorites, qui peuvent être envisagées actuellement comme des silicates phylliteux hydratés, dont le feuillet élémentaire d'une épaisseur voisine de 14 Å. résulte de l'association d'un feuillet mica et d'un feuillet brucitique. La plupart des minéraux, considérés comme chlorites par les anciens auteurs, possèdent cette structure. Cependant, un certain nombre d'entre eux ne présentent pas ces caractéristiques. Inversement, des minéraux à facies cryptocristallins ont pu être rattachés aux leptochlorites.

Nous examinerons tout d'abord quelques espèces, dont la détermination a paru douteuse, telles que la cronstedtite, l'amésite et les chlorites des minerais de fer.

Étude de quelques cas litigieux.

1. *Cronstedtite.*—S. B. Hendricks (10) à la suite d'une étude cristallographique détaillée, a conclu que la cronstedtite était un minéral à 7 Å., et de ce fait devait être retirée du groupe des chlorites et rapprochée de celui des kaolinites-antigorites.

Ceci implique une conséquence très importante au point de vue chimique. Il faut, en effet, que dans le feuillet kaolinitique de ce minéral, environ un ion Si sur deux soit remplacé par du fer trivalent. Le déficit de charges ainsi créé est en grande partie compensé par un excès de charges positives, dans la couche octaédrique, grâce au remplacement d'un ion ferreux par un ion ferrique. Cependant, dans quelques échantillons, cette compensation n'est pas complète, et l'égalisation des charges semble s'effectuer par des ions situés à l'extérieur des feuillets, comme dans le mica ou la montmorillonite. D'autre part, il est surprenant que l'on n'ait pas trouvé de cas intermédiaire entre les kaolinites-antigorites, où les remplacements de Si sont à peu près nuls, et celui de la cronstedtite, où cette substitution est si importante.

Nous avons cherché à vérifier ce résultat, tout d'abord à l'aide de l'analyse thermique différentielle. La courbe de la cronstedtite du Cornwall (fig. 1, courbe I) est identique à celle d'une kaolinite (fig. 1, courbe II), avec, toutefois, l'absence du phénomène exothermique. Ceci est d'autant plus curieux qu'étant donnée l'abondance des ions divalents, on s'attendait à une similitude avec une courbe d'antigorite (fig. 1, courbe III.)

L'examen à l'aide des rayons X montre qu'il s'agit d'un minéral à 7 Å. Néanmoins, comme nous le verrons plus loin, cette constatation n'est pas suffisante pour affirmer que le feuillet fondamental a bien cette épaisseur. Nous avons chauffé le produit à 520° et observé une destruc-

tion du réseau, comme il est normal pour une phyllite à 7 Å. On peut donc avec S. B. Hendricks classer la cronstedtite parmi les kaolinites-antigorites.

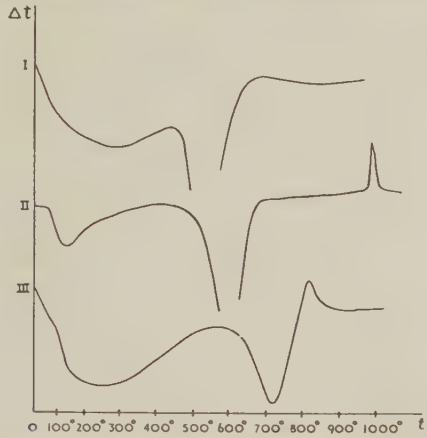

Fig. 1. Courbes thermiques différentielles: I, cronstedtite; II, kaolinite; III, antigorite; Δt, les différences de températures; *t*, la température en degrés Centigrades.

2. *Amésite.*—J. W. Gruner (11), à la suite d'une étude de l'amésite, a cru pouvoir, également, la classer dans cette dernière famille. Il est intéressant de signaler que tous les auteurs ont été frappés par les caractères de son diagramme aux rayons X. Déjà Ch. Mauguin (4) avait été conduit, tout en la maintenant parmi les chlorites, à admettre que son feuillet était constitué par deux éléments symétriques. De leur côté, R. C. McMurchy (6), et plus tard F. A. Bannister (12), l'avaient considérée comme une chlorite particulière.

Afin de vérifier ces déterminations, nous avons examiné le minéral de Chester: à l'état naturel, et après chauffage à 600°. On constate ainsi que le diagramme de l'amésite ne présente à 14 Å. qu'une raie très peu intense, alors que la raie à 7 Å. est, au contraire, fortement marquée. Après chauffage, le produit fournit un diagramme possédant une raie à 14 Å. très intense, mais les ordres immédiatement supérieurs ont disparu. Nous avons montré qu'un tel comportement est caractéristique des chlorites (13), (14). Ce fait a été, également, observé par G. W. Brindley (15). Nous conclurons que l'amésite est bien une chlorite.

3. *'Chlorites' des minerais de fer.*—Parmi les minéraux qui ont fait l'objet d'études récentes, il faut citer, également, les silicates associés aux minerais de fer sédimentaires. Ce sont, évidemment, des composés ferrifères. Comme nous l'avons déjà signalé, W. von Engelhardt (8) a précisé la façon dont les feuillets fondamentaux étaient juxtaposés.

D'après ses résultats, l'intensité relative des raies de la série (001) varie considérablement d'un type à un autre. Cependant, en général, on peut noter une tendance à l'affaiblissement du premier ordre par rapport aux chlorites normales, tel que le clinochlore. Par exemple, le diagramme d'une chamosite de Chamoson présente une raie (001) d'intensité presque nulle. Nous avons pu, cependant, montrer qu'ici encore, par chauffage à température convenable, on obtenait, comme dans le cas de l'amésite, un renforcement considérable de la raie (001), alors que les raies (002), (003), (004) disparaissaient totalement. Par ailleurs, les courbes thermiques différentielles et dilatométriques de ces minéraux correspondent bien à celles des chlorites. Vers la même époque, G. W. Brindley (15) décrivait un échantillon de chamosite à 7 Å., alors que nous-mêmes (14) constations que la berthiérine pouvait être rattachée aux antigorites.

4. *Chlorites artificielles.*—Les caractères des différentes raies (00l) observées avec les minéraux ferrifères ont pu être retrouvés dans les diagrammes de produits artificiels obtenus en précipitant divers hydroxydes au contact de la montmorillonite. On constate, en particulier, un affaiblissement de la raie (001), quand on passe d'une montmorillonite sur laquelle on a fixé $Al(OH)_3$ à une montmorillonite ayant fixé $Ni(OH)_2$ ou $Co(OH)_2$. Entre ces extrêmes se situent les substances préparées avec $Mg(OH)_2$ ou des mélanges de $Mg(OH)_2$ et de $Fe(OH)_2$. Pour caractériser ces chlorites artificielles et les distinguer des montmorillonites, on a d'abord vérifié que l'équidistance (001) restait stable par chauffage. D'autre part, elles se différencient des montmorillonites, car elles ne présentent pas de gonflements intracristallins par immersion dans l'eau. Toutefois, dans certaines conditions de préparation, telles que la précipitation de $Mg(OH)_2$ par la soude, on obtient des produits ayant un comportement normal à la chaleur, mais montrant dans l'eau un gonflement analogue à celui de la montmorillonite (16). De telles substances ont été trouvées peu de temps après dans le milieu naturel par D. M. C. MacEwan et S. S. Honeyborn (17). En se basant sur leurs caractères cristallographiques, il semble que ces minéraux doivent être inclus dans le groupe des chlorites. Leur particularité est de contenir des ions Na, Ca ou K compensant les déficits de charges du réseau. Nous envisagerons plus loin ce problème, mais dès à présent on peut concevoir, étant donnés ces résultats, qu'il sera possible de les maintenir dans le groupe des chlorites.

Composition chimique des chlorites.

Sur la seule base chimique, la classification consistait à définir des rapports entre les groupes d'éléments considérés comme équivalents.

L'utilisation de la composition chimique d'un corps, dont la structure est connue, conduit actuellement à faire d'autres rapprochements. Il faut en effet envisager les ions suivant les positions qu'ils peuvent occuper dans la structure (tétraédrique, octaédrique ou même hors du réseau). Sur cette base il devient possible, dans une certaine mesure, de localiser les éléments et d'en déduire une classification. Une formule représentant schématiquement les propriétés d'une chlorite peut s'écrire de la façon suivante: $Mg_3(Si,Al)_4O_{10}(OH)_2$ pour le feuillet mica avec Si/Al de 3 à 1, et $(Mg,Al)_3(OH)_6$ avec Mg Al de 2 à 1/2. Si on ne tient pas compte des molécules d'eau qui sont des éléments électriquement neutres, les ions métalliques sont liés à 14 oxygènes. Ils se répartissent ainsi: 4 en position tétraédrique et 2 fois 3 en position octaédrique, soit dans le feuillet mica, soit dans le feuillet brucitique. Le fait qu'une partie seulement d'entre eux peut se placer en position tétraédrique permet de faire un choix dans les constituants et de définir certaines caractéristiques du feuillet mica de la chlorite. C'est sur cette remarque que nous allons baser notre classification.

On calculera en molécules la composition chimique exprimée en oxydes d'un échantillon donné. Cette opération faite, on déterminera le nombre total d'oxygènes et d'ions métalliques de chaque type. Puis, on ramènera à 14 le nombre d'ions oxygène, en multipliant le total par un coefficient approprié. Le nombre d'ions métalliques de chaque type sera ensuite multiplié par le même coefficient. On obtiendra ainsi la quantité définitive des divers ions formant la maille. Tous les silicium seront considérés comme étant situés en position tétraédrique. Leur nombre est toujours inférieur à 4, et parfois dans une très large mesure. Il faut alors occuper le reste des positions tétraédriques en utilisant le titane, l'aluminium, le fer trivalent et le chrome. On constituera ensuite la couche brucitique en choisissant parmi les éléments disponibles. Il faut remarquer que non seulement toutes les positions octaédriques de cette couche doivent être utilisées, mais que le feuillet doit de plus présenter un excédent de charges compensant le déficit créé par la substitution. Aussi commencerons-nous par y incorporer une quantité d'éléments trivalents égale à celle existant en position tétraédrique. Si l'on complète à 3 unités avec des éléments divalents, tels que Mg,Fe^{11},Ni on aura ainsi une couche présentant un excès de charge. En effet, il suffit que ces positions soient occupées par des ions divalents pour que les charges des OH^- formant l'armature de l'hydroxyde soient compensées. Les ions trivalents présents créent donc un excès de charges positives. Quant aux constituants non utilisés, on les considérera comme formant la

couche octaédrique normale dans le feuillet mica. C'est-à-dire qu'il y aura 2 éléments trivalents ou 3 éléments divalents occupant les positions octaédriques. Cette méthode avait déjà été utilisée par J. Holzner (18) au cours d'une étude des chlorites ferrifères. Elle présente un élément d'arbitraire. En effet, rien ne permet d'affirmer que la compensation des charges ne s'effectue pas dans les deux couches octaédriques.

Cependant, on peut admettre un excès partiel des charges; en effet, nous avons déjà eu l'occasion d'attribuer à cet excès la température relativement élevée à laquelle se décompose le feuillet brucitique (19). Un deuxième point également remarquable, c'est que par attaque chimique il ne semble pas que cet élément de la structure soit plus rapidement détruit que la couche octaédrique du feuillet mica (20). Enfin, le feuillet brucitique avec son excès de charges joue, vis-à-vis de la chlorite, le même rôle que les tenons potassium vis-à-vis du feuillet mica. En appliquant cette méthode d'interprétation aux analyses des chlorites, il arrive que l'on ne puisse pas reconstituer normalement la structure. Nous négligerons les données analytiques douteuses, mais parmi celles qui paraissent correctes, deux cas peuvent se produire: il s'agit ou bien d'un minéral différent de la chlorite, ou bien d'une phyllite à rapprocher des chlorites 'gonflables'. Dans ce dernier cas, la quantité d'éléments trivalents nécessaires pour compléter le déficit de charges du feuillet mica est insuffisante.

L'analyse fait alors souvent apparaître la présence d'ions alcalins Na, K ou alcalino-terreux Ca dont le diamètre est trop grand pour qu'ils puissent se loger dans la structure. Ces éléments compensent le déficit de charges du feuillet mica et doivent se situer dans les cavités hexagonales de celui-ci. Il semble que parfois le rôle compensateur soit joué par des ions Mg, ceux-ci étant en excès sur le nombre de positions disponibles dans la structure. J. W. Gruner (11) a d'ailleurs attribué les anomalies de densité de quelques chlorites, dans ce cas, à une telle localisation d'ions Ca. Il s'agissait d'ailleurs de compenser une quantité d'eau insuffisante traduisant le déficit de charges positives dû au manque d'ions H.

Quant aux minéraux qui figurent indûment dans le groupe des chlorites, on peut essayer de les définir en calculant leur structure sur la base d'un feuillet de mica. C'est ainsi que la griffithite de Griffith, l'épichlorite de Derbyshire (16), la diabantite de Bergen Hill se classent dans les groupes des vermiculites ou des saponites (21). Dans le cas de ce dernier minéral, nous avons d'ailleurs pu vérifier que son équidistance (001) s'accroissait après immersion dans le glycérol, alors que par chauffage

elle se trouvait ramenée à l'équidistance fondamentale d'un mica. Ce comportement est donc analogue à celui d'une montmorillonite. Ainsi, sur la seule base chimique est-il possible de confirmer ou même d'établir l'appartenance d'un mineral à un type structural donné. Cependant, A. Hallimond (22) a montré que la présence de 5 % d'impuretés ne modifiait pas d'une manière considérable le résultat. Il faut donc une quantité notable de matières étrangères pour que cette méthode les mette en évidence.

L'eau dans les chlorites.

Les calculs effectués jusqu'à présent supposent implicitement que la teneur en eau est normale, ou, en d'autre termes, que les ions métalliques sont entourés par le nombre d'OH nécessaire pour constituer des feuillets de l'hydroxyde.

Théoriquement, trois H_2O complètent le feuillet brucitique, et un H_2O se trouve dans le feuillet mica.

Dans quelques cas, afin de vérifier si les quantités mesurées correspondaient aux valeurs théoriques, les pertes d'eau ont été déterminées à l'aide de la thermobalance Chèvenard.[1]

Les résultats de cette comparaison sont présentés dans le tableau suivant:

Minéral.	Théorique.	Trouvée.
Sheridanite de Comberousse	12·6	12·8
Clinochlore de Besafotra	12·7	12·5
Leuchtenbergite de Midongy	13·2	13·3

On constate que les valeurs expérimentales sont assez voisines des valeurs théoriques et, par conséquent, la composition chimique est normale.

Dans le cas de produits riches en fer ferreux, on peut noter deux singularités: d'une part la perte d'eau apparente, déterminée à la thermobalance, est très inférieure à la valeur théorique, d'autre part la courbe ne présente plus les deux inflexions correspondant aux départs d'eau successifs. [Le déficit de perte de poids constaté a été attribué (2) à la fixation d'oxygène par l'oxyde ferreux formé au moment de la déshydratation (23). De nouvelles mesures effectuées en chauffant la chlorite dans un courant d'oxygène et en recueillant l'eau dans l'acide sulfurique, ont permis d'établir, là encore, que sa teneur est voisine de la valeur théorique.]

[1] La thermobalance Chèvenard est un appareil qui permet d'enregistrer photographiquement, d'une manière continue, les variations de poids d'un échantillon en fonction de la température.

	Teneur en eau %		
Minéral.	Thermobalance.	Dosage direct.	Valeurs théoriques.
Bavalite	5·5	10·95	10·6
Thuringite	6·0	10·95	10·5
Métachlorite	6·0	11·4	10·8*
Ripidolite	7·8	12·0	11·9

* Calcul effectué à partir de l'analyse d'une métachlorite d'un autre gisement.

Il n'a pas été possible, même en recueillant l'eau, d'établir l'existence d'un double départ. En fait, les chlorites peu ferrifères donnent des courbes d'allure assez différente quant à leur pente. Pour certaines, la déshydratation se produit dans un intervalle de températures de quelques dizaines de degrés, alors que pour d'autres, ce phénomène s'étale sur plus de 100° C. Dans ce dernier cas, les deux départs ont tendance à se confondre.

On peut attribuer à la même cause l'inflexion unique des courbes des chlorites ferrifères. On pourrait vérifier cette hypothèse en recueillant l'eau, mais il faudrait opérer sur de très petits intervalles de températures et la méthode deviendrait fort laborieuse.

L'analyse thermique différentielle met généralement en évidence l'existence de deux crochets, mais ceci ne nous apprend rien sur l'allure des courbes thermopondérables, puisque cette méthode thermique différentielle fait apparaître un aspect énergétique qui est exclu de la mesure pondérale.

On sait d'ailleurs que l'inflexion due au départ de l'eau hygroscopique de la montmorillonite Ca ne présente pas de singularité marquée quand on l'étudie à la thermobalance, alors qu'il se produit un dédoublement accentué à l'analyse thermique.

On n'a pas pu établir de corrélation entre la composition chimique (en particulier l'existence de déficits de charges locaux) et la température des départs d'eau. Ceci, aussi bien en mesurant les températures à l'aide de la thermobalance que par l'analyse thermique différentielle. Il n'est pas exclu, cependant, qu'une telle influence existe, mais l'effet produit est probablement inférieur à la précision des mesures.

Seule l'influence du fer ferreux est considérable. En effet, les chlorites ferrifères peuvent perdre leur eau à 200° de moins que les produits alumineux et magnésiens correspondants.

Classification.

La méthode de calcul développée précédemment permet d'établir, dans une certaine mesure, la constitution du feuillet mica. Celui-ci se trouve caractérisé par le déficit de charges **a** dû au remplacement du

silicium par des éléments trivalents, si l'on admet le postulat que Si est toujours en position tétraédrique.

L'importance de la substitution **a** est alors nécessairement définie, le nombre de Si présent étant $4-a$.

Associant ainsi les données de la cristallographie aux résultats de l'analyse chimique, on peut établir un système de classification. Il est équivalent à l'ancien quant à son principe, mais on choisit comme caractère distinctif la teneur en silicium, $4-a$. La constitution d'un certain nombre de chlorites a été calculée d'après ces principes, et les minéraux répartis dans quatre groupes.

Comme la base de cette classification porte sur la constitution du feuillet mica de la chlorite, on peut donc comparer les feuillets ainsi calculés à ceux des micas. C'est pourquoi dans le tableau ci-dessous, en face des limites indiquées, figure le nom d'un mica dont le feuillet a une constitution identique.

		Teneur en ions Si	
Amésite	Groupe I	2 à 2·2	margarite
Prochlorite	Groupe II	2·3 à 2·8	lépidomélane
Clinochlore	Groupe III	2·9 à 3·05	muscovite
Pennine	Groupe IV	3·05	séricite, montmorillonite

Groupe I.

Nombre d'ions Si 2 à 2·2 Nombre d'ions Fe 0·67 à 1·28

Amésite

Groupe II. Nombre d'ions Si 2·3 à 2·8

Nombre d'ions Fe

0 à 1	1 à 2	> 2
héridanite	Chlorite (grochauite)	Thuringite
Comberousse, France	des marundites	Chester Co., Pennsylvania
rochauite	Corundophilite	Thuringite
Carter Mine, North Carolina		Messina, Transvaal
euchtenbergite		Ripidolite
Ambatofinandrahana, Madagascar		Masoala, Madagascar
rochauite	Ripidolite	Ripidolite
Antohidrano, Madagascar	Androta, Madagascar	Laifour, Ardennes, France
	Ripidolite	Aphrosidérite
	Col de la Croix, France	Weilburg, Nassau
		Thuringite, Evisa, Corse
		Epichlorite
		Elbingerode, Harz
		Bavalite
		Bas-Vallon, France
		Thuringite
		Schmiedefeld, Thuringia
index de réfraction:	1·57 à 1·59 1·593 à 1·62	1·63 à 1·67
a pesanteur spécifique:	2·68 à 2·75 2·79 à 2·90	2·96 à 3·20

GROUPE III.

Nombre d'ions Si 2·9 à 3·05

Nombre d'ions Fe*	
0·0 à 1	2
Chlorite blanche de Mauléon, France	Delessite Batoum, Caucase
Clinochlore Bernstein, Austria	Chamosite Windgalen, Switzerland
Kotschubéite Ufaleisk, Urals	
Kotschubéite Patevi, Togo	
Clinochlore Besafotra, Madagascar	
Kotschubéite Hagdale, Shetland	
L'index de réfraction: 1·57 à 1·583	1·60 à 1·64
La pesanteur spécifique: 2·67 à 2·70	2·80 à 3·40

* Il n'y a pas de minéraux pour lesquels le nombre d'ions Fe reste entre 1 et 2.

GROUPE IV.

Nombre d'ions Si > 3·05

Nombre d'ions Fe*	
0 à 1	2
Leuchtenbergite Midongy, Madagascar	Diabantite Reinsdorf, Saxony
Pseudophite South Africa	Diabantite Farmington Hill, Connecticut
Pennine Zermatt, Switzerland	Diabantite Trillochthal, Saxony
Pseudophite Nassfeld, Austria	
L'index de réfraction: 1·572 à 1·577	1·62 à 1·65
La pesanteur spécifique: 2·66 à 2·67	2·9 à 3

* Il n'y a pas de minéraux pour lesquels le nombre d'ions Fe reste entre 1 et 2.

General Résumé

The classification of the chlorites is now based upon four groups:

Group I is probably rare and so far is represented only by amesite.

Group IV comprises more numerous elements, but besides normal chlorites, like pennine and leuchtenbergite, there are also a certain number of imperfect minerals, especially the 'inflatable' chlorites (17).

This classification results in dividing the chlorites into coherent groups,

o which can be compared with mica types. This last result is particularly nportant, since it seems that in nature a certain number of these minerals t 14Å. result from the transformation of phyllites at 10 A. or are found losely associated with them (see footnote, p. 329).

In order to introduce subdivisions, we shall choose as our second riterion, the nature of the constituents. As chlorites are normally ormed by aluminous and magnesium ions, it will be enough if we con- ider the proportion of elements other than these, such as Fe, Mn, or Ni, o obtain a definition of the types. In the minerals we have studied, iron ione is to be found in any quantity; so we have not had to consider any ther ions. In general, if we compare the results of this attempt at assification with that made on a purely chemical basis, we may notice certain parallelism. Thus amesite remains characteristic of the type ch in alum; Group II covers the whole of groups 2–3–4 of Orcel's arlier classification comprising corundophilites, grochauites, ripidolites, pichlorites, bavalite, and thuringite. Group III, clearly equivalent to roups 5 and 6, comprises clinochlores, delessite, and chamosite. Finally, n Group IV, we come across elements 7 and 8 of the preceding classifica- on; that is, pennines, diabantites, and pseudophites. Only a few minerals re displaced to any extent, for example, certain leuchtenbergites pass- ng from groups 3 and 4 to Group IV.

The essence of any classification is that it should have, at least mplicitly, a genetic significance. The correspondence which we have ndicated between the chlorite and the mica groups seems to indicate nat this condition is observed. Besides this, it is evident that to a given lace, in the classification, a whole series of properties should correspond. his seems to be the case. Indeed, in each group, types are classed by efraction indexes and increasing densities. This is clear from the values ndicated below the tables. The phenomena of reoxidation, and, as a esult, the difference between the apparent loss of weight and the water ontent, corroborate it. On the other hand, the water content and the emperature at which dehydration takes place decrease as the iron con- ent increases. Finally, it is likely that some other properties should be assed in the order already indicated; thus, colour will range from light nts, near to white, to dark greens, almost black, as we pass from type 1 o type 3, in each group. On the other hand, dielectric properties will ecessarily decrease in the same direction.

In short, the proposed classification, if it does not permit us to account r all the properties which may attract the attention of the mineralo- st, groups the chlorites in accordance with their essential properties.

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Paralaurionite[1]

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Abstract: Paralaurionite from a new locality, the Mammoth mine, Arizona, is described. X-ray study and chemical analysis confirm the original characteristics of the mineral as described in 1899 by G. F. Herbert Smith. Measurements are given which establish new forms on crystals from Arizona and also on crystals from a South American locality. A complete angle table for twenty-eight forms is presented.

THIS rare oxychloride of lead was first described from the lead slags of Laurium, Greece, by G. F. Herbert Smith in this magazine in 1899. In the same year the mineral rafaelite was reported by Arzruni from Mina San Rafael, Sierra Gorda, Chile, but Smith quickly established the identity of the two substances. It proved to be not uncommon at Laurium, as shown by Descloizeaux and others. The proposal of Ktenas to consider it identical with laurionite whose orthorhombic form he thought due to submicroscopic twinning of plates of paralaurionite has not been accepted. Russell described its sparse occurrence at a locality in Cornwall. Except for a review of previous studies with some new observations by the writer, nothing has since been added to our knowledge of paralaurionite. This review, which includes full references to all papers above mentioned, appeared in this magazine in vol. 23, p. 573, 1934.

About 1942 paralaurionite was identified in a suite of minerals from the Mammoth mine, Tiger, Arizona. It was fairly abundant and was well crystallized. The following pages present the results of a study of these specimens; at the same time measurable crystals of so-called rafaelite were found on a specimen of percylite labelled Caracoles, Bolivia (?), in the Harvard Mineralogical Museum, and the measurements made upon them are also presented here.

Paralaurionite from the Mammoth mine.

The complex of lead and copper minerals found in the Collins vein of the Mammoth mine between the 300-foot and the 700-foot levels was preserved in very numerous specimens of which the Harvard Museum secured a fairly representative series. It includes galena and chalcocite, the original ores, in the form of remnants surrounded by oxidation products; for the most part the minerals present are secondary and in bewildering variety. No description of the suite as a whole has appeared

[1] Contribution from the Department of Mineralogy and Petrography, Harvard University.

in print; Dr. Harry Berman and the writer were engaged in their study when war intervened and Berman's untimely death in 1944 brought our work to an end. Only the three species diaboleite (1), dioptase (2), and wherryite (3) have been described in any detail. An alphabetical list will at least give some idea of the paragenesis but none at all of the brilliant colours, superb crystallization, and infinitely varied groupings of these minerals. Besides the primary sulphides and quartz there have been found:

Anglesite	Cerussite	Hemimorphite	Paralaurionite
Atacamite	Descloizite	Hydrocerussite	Phosgenite
Azurite	Diaboleite	Leadhillite	Vanadinite
Boleite	Dioptase	Linarite	Wherryite
Brochantite	Embolite	Malachite	Willemite
Caledonite	Fluorite	Matlockite	Wulfenite

Paralaurionite is one of the later minerals in this series. It occurs in slender isolated needles in cavities of cerussite; and in coarser crystal aggregates, especially with leadhillite. The most notable specimen in our collection (101132) shows a surface 3 by 2 inches covered with bladed crystals of paralaurionite up to an inch in length and half an inch thick, which show well the characteristic fibration due to gliding under pressure. On them is a later generation of leadhillite.

No twin crystals were observed, a marked contrast to those from Laurium; and, too, the crystals, unlike the flat plates of Laurium, are elongated in the direction of the symmetry axis either as needles or as plates parallel to the pinacoid (100). Nine crystals were measured, all being set on the goniometer with the symmetry or *b*-axis vertical; that is, in the position of second inversion so that the resulting measurements are the angles ϕ_2 and ρ_2 of the form table. Their very high lustre resulted in reflections of the finest quality, so that even most minute facets gave accordant readings.

Paralaurionite, 'rafaelite', from Caracoles, Bolivia (?)[1]

The specimen is a fairly large fragment consisting of massive dark blue percylite mixed with siliceous gangue matter; in small cavities tiny crystals of paralaurionite project from the walls. They have the pale lilac colour described as characteristic of the original rafaelite and the same elongation parallel to the symmetry axis. They were measured in the same position as were the Arizona crystals.

[1] The label of specimen no. 95812 is so given, but Bolivia is believed to be a mistake for Chile. No such locality as Caracoles was discoverable on our maps of Bolivia. On the other hand, the well-known mining locality of that name in Chile was probably the source of the original rafaelite.

Tabular presentation of the results of crystal measurements.

Table I shows the combinations of forms observed on the nine crystals from Arizona and the seven from South America measured. The last column gives the relative abundance of each form, including the only other important locality for the mineral, Laurium, Greece. The eleven new forms include several that are as common as those previously known.

TABLE I. Paralaurionite: combinations and frequency of forms.

Form.		Measured crystals. Arizona 9 cryst.									Chile 7 cryst. 'Rafaelite'.							General frequency, all localities.
	001	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	On all crystals
	010				x	x			x	x								Very rare
	100	x	x	x	x	x	x		x	x	x	x	x	x	x	x	x	On most crystals
*	140		x									x	x			x	x	Rare
n	110		x		x	x		x	x	x	x	x	x	x	x	x	x	On most crystals
	310										x	x	x	x	x	x	x	Rafaelite only
*	203										x			x				,, ,, v. rare
	201											x		x	x	x	x	,, ,,
	401											x				x	x	,, ,,
*	$\bar{1}02$													x	x			,, ,, v. rare
g	$\bar{2}03$	x	x		x	x		x			x				x	x	x	Common form
	$\bar{1}01$	x	x		x			x	x	x	x	x		x	x	x	x	,, ,,
*	$\bar{4}03$	x			x	x		x									x	Rare
n	$\bar{2}01$	x	x	x	x	x	x	x	x	x	x	x		x	x	x	x	On most crystals
w*	$\bar{3}01$	x			x	x		x	x	x								Arizona only
	$\bar{4}01$	x	x	x	x	x					x			x	x	x		Common form
	$\bar{5}01$			x														Very rare
	601	x	x	x	x	x	x			x	x				x		x	Common form
*	112		x		x	x				x								Arizona only—rare
p	111	x	x	x	x	x	x			x	x	x	x	x	x	x	x	On most crystals
O*	$\bar{1}12$				x			x	x	x	x					x		Common form
P*	$\bar{1}11$	x	x		x		x		x	x	x							,, ,,
y	411										x	x	x	x	x	x	x	Rafaelite only, common
	511							x	x									Rare form
S*	$\bar{3}11$				x	x					x	x	x		x	x		Common form
T*	$\bar{5}11$			x	x	x	x	x	x	x								Arizona only
U*	$\bar{7}11$										x	x	x	x		x		Rafaelite only

* Indicates forms new to the species.

Table II contains the mean measured angles of the new forms, together with the range in position of each. Observed angles of forms previously known are not given. They were in excellent agreement with calculated angles.

TABLE II. Paralaurionite: measured angles of new forms (in position of 2nd inversion)

Form.	No. of faces.	Qual.	Mean Position. ϕ_2	Mean Position. ρ_2	Range. ϕ_2	Range. ρ_2
r 140	5	good	0°00′	5°57′	0 00	5°50′–6°11′
s 203	3	good	44 26	90 00	44°34′–45°30′	90 00
u $\bar{1}02$	3	fair	820 7½	90 00	82 00–82 08	90 00
v $\bar{4}03$	5	poor	115 45	90 00	115 32–115 50	90 00
w $\bar{3}01$	8	fair	149 54	90 00	149 30–150 10	90 00
o 112	4	poor	48 20	56 03	48 07–48 38	55 45–56 25
O $\bar{1}12$	4	good	82 06½	48 13	81 33–82 43	47 55–48 36
P $\bar{1}11$	5	good	103 13	29 43	102 48–103 38	29 28–30 17
S $\bar{3}11$	7	good	150 06	48 00	149 25–151 01	47 48–48 14
T $\bar{5}11$	7	v. good	162 45	61 59	162 23–162 57	61 47–61 58
U $\bar{7}11$	6	good	168 03	69 29	167 28-168 34	69 00–69 40

TABLE III. Paralaurionite, Pb(OH)Cl; angle table.

Monoclinic prismatic, $2/m$.

$a : b : c = 2{\cdot}7052 : 1 : 1{\cdot}8090$, $\beta = 117° 12\frac{1}{2}'$; $p_0 : q_0 : r_0 = 0{\cdot}6687 : 1{\cdot}6088 : 1$; $r_2 : p_2 : q_2 = 0{\cdot}6216 : 0{\cdot}4157 : 1$, $\mu = 62° 47\frac{1}{2}'$; p_0' 0·7519, q_0' 1·8090, x_0' 0·5142.

Forms		ϕ	ρ	ϕ_2	ρ_2 = B	C	A
c	001	90°00′	27°12½′	62°47½′	90°00′	—	62°47½′
b	010	0 00	90 00	—	0 00	90°00′	90 00
a	100	90 00	90 00	0 00	90 00	62 47½	0 00
r*	140	5 56	90 00	0 00	5 56	87 17½	84 04
m	110	22 34½	90 00	0 00	22 34½	79 53½	67 25½
n	310	51 16½	90 00	0 00	51 16½	69 06	38 43½
s*	203	90 00	45 26½	44 33½	90 00	18 14	44 33½
e	201	90 00	63 38½	26 21½	90 00	36 26	26 21½
f	401	90 00	74 09	15 51	90 00	46 56½	15 51
u*	$\bar{1}02$	90 00	7 52½	82 07½	90 00	19 20	82 07½
g	$\bar{2}03$	90 00	0 44½	89 15½	90 00	26 28½	89 15½
d	$\bar{1}01$	−90 00	13 22½	103 22½	90 00	40 35	103 22½
v*	$\bar{4}03$	−90 00	26 01½	116 01½	90 00	53 14	116 01½
h	$\bar{2}01$	−90 00	44 42	134 42	90 00	71 54½	134 42
w*	$\bar{3}01$	−90 00	60 08	150 08	90 00	87 20½	150 08
k	$\bar{4}01$	−90 00	68 09	158 09	90 00	95 21½	158 09
i	$\bar{5}01$	−90 00	72 52½	162 52½	90 00	100 05	162 52½
l	$\bar{6}01$	−90 00	75 57½	165 57½	90 00	103 10	165 57½
j	$\bar{8}01$	−90 00	79 42	169 42	90 00	106 54½	169 42
o*	112	44 32½	51 45½	48 19½	55 57½	36 38½	56 34
p	111	34 59½	65 38	38 18	41 43½	52 43	58 30½
O*	$\bar{1}12$	8 41½	42 27½	82 07½	48 08½	45 21	84 09
P*	$\bar{1}11$	−7 29	61 16½	103 22½	29 36½	67 58	96 33½
y	411	62 49	75 49½	15 51	63 42½	52 15½	30 24½
t	511	67 03½	77 50½	13 10	67 36	53 12	25 48½
S*	$\bar{3}11$	−43 54½	68 17	150 08	47 59	88 01½	130 07
T*	$\bar{5}11$	−60 52	74 56	162 52½	61 57½	81 07	147 30½
U*	$\bar{7}11$	−69 09	78 52	168 06½	69 33½	104 20	156 29

Table III is a complete angle table for paralaurionite, none of this

type having hitherto been printed. It will be observed that the position and values of the crystal elements are those originally chosen by Smith, the correctness of this choice having been established by X-ray study.

The constants of the unit cell were determined by C. W. Wolfe (1945), in the Harvard Laboratory by the Weissenberg method. Space-group $C\,2/m$; $a_0 = 10{\cdot}77$, $b_0 = 3{\cdot}97$, $c_0 = 7{\cdot}18$kX, $\beta = 117°\,13'$, hence $a_0 : b_0 : c_0 = 2{\cdot}713 : 1 : 1{\cdot}809$. Compare with these figures the morphological axial ratio $a : b : c = 2{\cdot}7052 : 1 : 1{\cdot}8090$, $\beta = 117°12\frac{1}{2}'$. Unit-cell contents $Pb_4(OH)_4Cl_4$.

Chemical composition.

The chemical composition of the Arizona paralaurionite was established by the analysis of column I below, made in 1948 by F. A. Gonyer of the Harvard staff. The calculated composition for the accepted formula, Pb(OH)Cl is given in column II.

			I	II
Pb	...	...	77·75	79·80
O	...	...	6·00	3·08
Cl	...	...	12·84	13·65
H_2O	...	...	3·51	3·47
			100·10	100·00

I am indebted to Dr. C. W. Wolfe for the drawing of the crystal and for the X-ray measurements; and to Mr. Forest A. Gonyer for the chemical analysis.

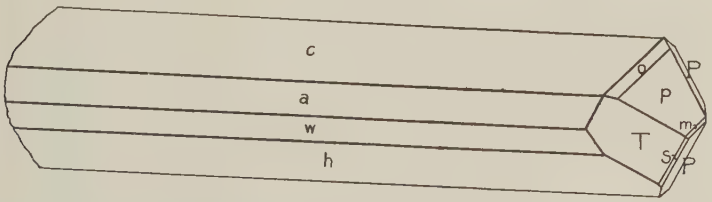

FIG. 1. Crystal of paralaurionite from Arizona. Forms: *c* 001, *a* 100, *m* 110, *h* $\bar{2}01$ *w* $\bar{3}01$, *o* 112, *p* 111, *P* $\bar{1}11$, *S* $\bar{3}11$, *T* $\bar{5}11$, of which *w*, *o*, *P*, *S*, and *T* are new.

References: (1) Diaboleite. C. Palache. Amer. Min. 1941, vol. 26, p. 605. [M.A. 8–215.]

(2) Dioptase. F. W. Galbraith and T. H. Kuhn. Ibid., 1940, vol. 25, p. 708. [M.A. 8–224.]

(3) Wherryite. J. J. Fahey, E. B. Daggatt, and S. G. Gordon. Ibid., 1950, vol. 35, p. 93. [M.A. 11–127.]

Studies of mineral sulpho-salts: XV. Xanthoconite and pyrostilpnite[1]

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IN his long conduct of the *Mineralogical Magazine* and *Mineralogical Abstracts* our Editor has always shown a ready interest and understanding for each new phase of mineralogy as it has appeared, and thus a contribution to any part of the wider realm of mineralogy would fall in the range of Dr. Spencer's comprehending appraisal. At the same time Dr. Spencer's own published work in mineralogy and the style of his abstracts of the works of others show that his personal interests incline to the classical natural history aspect of mineralogy, which gives first importance to exact observations that establish the individuality of new species, improve and extend the knowledge of well-defined species, or disprove the existence of supposed new minerals. And, therefore, in choosing a topic for this collection of papers in which we seek to honour our Editor and emphasize his influence on mineralogy, I have resisted an urge to wander from the straight path of descriptive mineralogy and have decided to bring together some notes, already a few years old, on a pair of still imperfectly known mineral sulpho-salts.

Xanthoconite, $3Ag_2S.As_2S_3$, and pyrostilpnite (fireblende), $3Ag_2S.Sb_2S_3$, are the relatively rare, apparently monoclinic analogues of the ruby silvers, proustite and pyrargyrite. Both of the rarer species are known only as small imperfect crystals, and consequently there are crystallographic uncertainties which are best resolved by X-ray measurements. In anticipation of this paper the results of such measurements were briefly stated in two notes (1943, 1947); but apart from these observations the descriptions of the two species, as given in Dana (1944), are substantially as they stood after the work of Miers (1893) on xanthoconite and Luedecke (1882) on pyrostilpnite.

[1] Contributions to Mineralogy from the Department of Geological Sciences, University of Toronto, 1950, no. 5. No. XIV of this series is by Robinson (1948); no. XIII, by Peacock and Berry (1947), appeared in this *Magazine*.

[2] The sad news of Professor Martin Alfred Peacock's sudden death on October 30 was received during the preparation of this number.

For the present work the following specimens were assembled:

1. Xanthoconite, Příbram, Bohemia (Harvard Mineralogical Museum, 94799); yellow crystals of thick tabular to short columnar pseudo-orthorhombic habit (fig. 1).
2. Xanthoconite ('rittingerite'), Joachimsthal, Bohemia (HMM 82544); yellowish tabular pseudo-orthorhombic crystals (fig. 2).

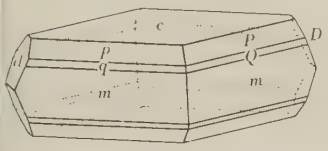

Fig. 1.

Fig. 2.

3. Xanthoconite, La Rose mine, Cobalt, Ontario (Royal Ontario Museum, M 14342); hemispherical crusts of minute buff crystals with occasional implanted crystals of proustite.
4. Pyrostilpnite, Příbram, Bohemia (HMM 94799); minute red laths, some twisted about the long edge.
5. Pyrostilpnite, Andreasberg, Harz (HMM 94802); stilbite-like group of minute red crystals (figs. 4, 5).
6. Pyrostilpnite, Randsburg, California; minute red lath-like crystals.

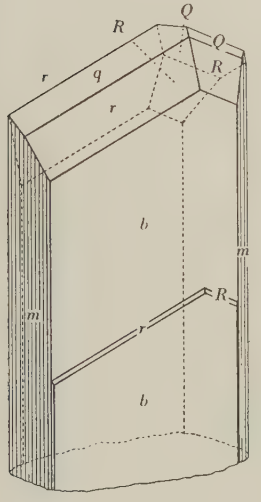

Fig. 4.

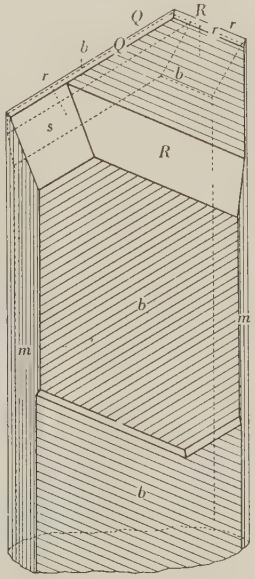

Fig. 5.

The specimens from the Harvard Mineralogical Museum were kindly lent for study by the late Dr. Harry Berman; the specimen from the

Royal Ontario Museum by Professor A. L. Parsons; and the crystals from California by Professor J. Murdoch (Los Angeles) who also sent me some unpublished two-circle measurements and a cell determination with permission to use them in this work. My thanks are also due to Dr. E. W. Nuffield who prepared the drawings for figs. 1–3 from my sketches, and to Dr. L. G. Berry who indexed the powder pattern of xanthoconite (table III).

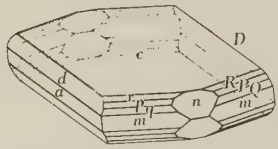

Fig. 3.

Xanthoconite.

Crystal lattice and morphology.—This is a case where sharp X-ray photographs on a small crystal may be expected to give better geometrical elements than those obtained by the reflecting goniometer. A small equant fragment was obtained from a crystal from material no. 1; this gave excellent signals from $c(001)$ and $D(\bar{5}01)$ of Miers, permitting accurate adjustment for rotation about [010], and poor signals from faces of the type (hhl). A rotation photograph and Weissenberg resolutions of the zero and first layer lines gave a monoclinic lattice in which the simplest cell is base centred, with symmetry of the space group $C2/c$ and the dimensions:[1]

$$a' = 11{\cdot}97,\ b' = 6{\cdot}20,\ c' = 16{\cdot}95\ \text{kX},\ \beta' = 110°\ 10'$$

using Cu–$K\alpha^1$ = 1·5374 kX. However, the typical habit of xanthoconite is pseudo-orthorhombic with frequently like development of (hhl) and $(\bar{h}hl)$ forms and common twinning on (001), further accentuating the nearly rectangular lattice. It seems proper, therefore, to choose the corresponding unit cell which is face-centred, with the symmetry $F2/d$ and the cell edges $a = [\bar{1}00]$, $b = [0\bar{1}0]$, $c = [102]$, which give:

$$a = 11{\cdot}97,\ b = 6{\cdot}20,\ c = 31{\cdot}82\ \text{kX},\ \beta = 90°\ 30\tfrac{1}{2}'.$$

This cell gives the following geometrical ratios as compared to Miers's final elements based on many old and new measurements:

$$a : b : c = 1{\cdot}9307 : 1 : 5{\cdot}1327\,;\ \beta = 90°\ 30\tfrac{1}{2}'\ \text{M. A. P. (X-ray)}$$

$$a : b : 5c = 1{\cdot}9187 : 1 : 5{\cdot}0760\,;\ \beta = 91°\ 13'\ \text{Miers (gon.)}.$$

The agreement is not good, but this is not surprising in view of the

[1] All the unit-cell dimensions and spacings in this paper are based on Cu-$K\alpha_1$ = 1·5374 kX and the calculated densities on the mass factor 1·650. In Å. as defined in 1947 the cell dimensions of xanthoconite are $a' = a = 11{\cdot}99$, $b' = b = 6{\cdot}21$, $c' = 16{\cdot}98$, $c = 31{\cdot}86$. M. A. P.

generally poor quality of the crystal faces which commonly do not allow a distinction to be made between (*hhl*) and ($\bar{h}hl$) forms.

The transformation, old (Miers) to new (M. A. P.), is simply 100/100/005, which gives the comparison of symbols of the reported forms in table I. The new setting gives a net simplification of indices, and some apparent complications (*t T h H y Y ρ*) in which the transformed indices are, however, close to simple indices.

TABLE I. Xanthoconite: reported forms in old and new notations.

Old.	New.	Old.	New.
a(100)	*a*(100)	*H*($\bar{3}34$)	$-(\bar{3}.3.20) \sim (\bar{1}17)$
c(001)	*c*(001)	*p*(111)	*p*(115)
m(110)	*m*(110)	*P*($\bar{1}11$)	*P*($\bar{1}15$)
n(053)	*n*(013)	*y*(443)	$-(4.4.15) \sim (114)$
d(501)	*d*(101)	*Y*($\bar{4}43$)	$-(\bar{4}.4.15) \sim (\bar{1}14)$
D($\bar{5}01$)	*D*($\bar{1}01$)	*ρ*(332)	$-(3.3.10) \sim (113)$
r(112)	*r*(1.1.10)	**u*(553)	*u*(113)
R($\bar{1}12$)	*R*($\bar{1}$.1.10)	**v*($\bar{5}53$)	*U*($\bar{1}13$)
t(223)	$-(2.2.15) \sim (117)$	**z*(552)	*z*(112)
T($\bar{2}23$)	$-(\bar{2}.2.15) \sim (\bar{1}17)$	*q*(551)	*q*(111)
h(334)	$-(3.3.20) \sim (117)$	*Q*($\bar{5}51$)	*Q*($\bar{1}11$)

* Tokody (1930).

Table II compares interfacial angles calculated from the X-ray elements with measurements given by Miers (1893), which include observations by Breithaupt, Schabus, Streng, and Schrauf, by Tokody (1930), and new measurements on two crystals from material no. 1. It will be seen that the calculated angles mostly lie well in the range of the measured angles, and that many individual measurements (often representing angles to planes whose symbols were not determined as positive or negative) agree closely with the calculated angles *c* : (*hhl*) or *c* : ($\bar{h}hl$). Thus the X-ray elements suit the geometrical observations well and, at the same time, the forms *a*(100), *c*(001), *m*(110), *n*(013), *d*(101), *D*($\bar{1}01$), *r*(1.1.10), *R*($\bar{1}$.1.10), *p*(115), P($\bar{1}15$), *u*(113), *U*($\bar{1}13$), *z*(112), *q*(111), *Q*($\bar{1}11$) are confirmed. We may accept Miers's statement that the common forms are *c m d D p P q Q*; and it seems proper to regard the forms *t T h H y Y ρ* (table I) as uncertain.

In keeping with the Bravais principle, when the vertical axis is much longer than the other axes, crystals of xanthoconite are always more or less tabular parallel to the base, which is also the plane of cleavage; and the gnomonic distances *h*/*l* of the (*hhl*) planes are terms of an harmonic series (1937):

$$c(0) \quad r(\tfrac{1}{10}) \quad p(\tfrac{1}{5}) \quad u(\tfrac{1}{3}) \quad z(\tfrac{1}{2}) \quad q(1).$$

But in detail there are many exceptions to the theoretical habit required

in the space-group $F2/d$ by the Bravais–Donnay–Harker principle (Donnay, 1946).

TABLE II. Xanthoconite: calculated and measured angles.

	Calculated.	Measured.
ca = (001) : (100)	89°29½′	88°37′–89°41′ M. A. P. (4)
am = (100) : (110)	62 37	62 18 –62 32 M. A. P. (6)
cm = (001) : (110)	89 46	89 42 –89 55 M. A. P. (4)
cn = (001) : (013)	59 41½	59 52 –60 09 M. A. P. (2)
cd or cD	—	68 14 –70 46 (17)
cd = (001) : (101)	68 56½	68 42 Miers
		68 54 Miers
cD = (001) : ($\bar{1}$01)	69 50	69 30 Breithaupt
		69 40 Streng
		69 49 M. A. P.
		69 57 Miers
		70 01 Miers
cr or cR	—	28 18 –31 32 (10)
cr = (001) : (1.1.10)	29 58	29 25 Schrauf
		30 00 Schabus
cR = (001) : ($\bar{1}$.1.10)	30 05½	30 04 Schrauf
		30 09 Miers
cp or cP	—	48 10 –50 25 (25)
		48 57 Tokody
cp = (001) : (115)	49 00	48 58 M. A. P.
		49 02 Miers
		49 03 Miers
		49 04 M. A. P.
		49 07 Streng
cP = (001) : ($\bar{1}$15)	49 16½	49 10 Schabus
		49 10 Schrauf
		49 10 Tokody
		49 17 Miers
		49 23 M. A. P.
cu = (001) : (113)	62 23	61 40 Tokody
cU = (001) : ($\bar{1}$13)	62 45½	62 51 Tokody
cz = (001) : (112)	70 42½	70 28 Tokody
cq or cQ	—	70 03 –81 30 (19)
cq = (001) : (111)	79 57½	79 25 Breithaupt
		79 39 M. A .P.
		79 59 Miers
		80 01 Miers
		80 08 M. A. P.
cQ = (001) : ($\bar{1}$11)	80 24½	80 26 M. A. P.
		80 46 Miers

Figs. 1–3 illustrate the principal habits of xanthoconite. Fig. 1 represents the two crystals from Příbram, Bohemia (material no. 1), on which the goniometric and X-ray measurements were made. Fig. 2 is the typical habit of the so-called 'rittingerite' from Joachimsthal, which was shown to be xanthoconite by Miers (1893) aided by Prior. Fig. 3,

which shows elongation with the *b*-axis, is based on Miers's plan of crystals from Freiberg; the artificial crystals described recently (1947) have a similar habit.

Unit-cell contents and density.—The base-centred cell with dimensions b' b' c' β', already given, contains

$$Ag_{24}As_3S_{24} = 4[3Ag_2S.As_2S_3],$$

while the face-centred cell a b c β has the double volume and cell content. The calculated density is 5·53, which affords striking verification of Prior's two sets of pyknometric determinations on 23 mg., which gave the specific gravities 5·68 and 5·40, average 5·54.

Optics and twinning.—The crystal used for X-ray measurements is yellow under the microscope, with no distinct pleochroism. It shows the emergence of a bisectrix nearly normal to the base and the optic axial plane normal to the symmetry plane. $2E$ is very large and the dispersion is very strong $r<v$. An entirely satisfactory determination of the sign was not obtained. In view of the very limited material no attempt was made to determine the refractive indices in melts of selenium and arsenic selenide, in which the crystals, like those of polybasite, would doubtless have dissolved. These observations confirm those of Miers, who also gave the optic sign as negative.

Miers also noted optical effects indicating twinning on (001). Our X-ray crystal showed little evidence for this under the microscope, but the Weissenberg photographs showed faint additional ($h0l$) spots exactly in positions required by twinning on (001). Evidently the crystal is in very small part twinned by reflection in the base, which is a plane of pseudo-symmetry in the F-lattice and consequently a probable plane of twinning.

X-ray powder pattern.—Samples from materials 1, 2, 3 all gave the same X-ray powder pattern. To aid in the identification of xanthoconite and perhaps eventually in the determination of the structure, the observations on the best film are given with the calculated spacings of the reflecting planes in table III.

Pyrostilpnite.

Crystal lattice and morphology.—In view of the uncertainty of the crystallography of pyrostilpnite—even the crystal system is doubtful—a determination of the crystal lattice was first made from X-ray photographs of a lath-shaped crystal from Příbram (material 4) rotated about the long edge of the lath. The simplest cell in the lattice is monoclinic,

space-group $P2_1/c$, with

$$a' = 6{\cdot}83,\ b' = 15{\cdot}81,\ c' = 6{\cdot}23\ \text{kX},\ \beta' = 117^\circ\ 09'.$$

The face of the lath is the symmetry plane, and the long edge is taken as the vertical axis, as in Luedecke's setting (1882). Fortunately the space-

TABLE III. Xanthoconite, $3Ag_2S.As_2S_3$; Joachimsthal, Bohemia, X-ray powder pattern. Monoclinic, $F2/d$. $a = 11{\cdot}97,\ b = 6{\cdot}20,\ c = 31{\cdot}82$ kX, $\beta = 90^\circ\ 30\frac{1}{2}'$; Z = 8.

I	θ(Cu)	d(meas.)(hkl)	d(calc.)	I	θ(Cu)	d(meas.)(hkl)	d(calc.)
			5·585			(222)	2·714
2	8·05	5·49 (202)	5·428	1	16·5	2·71 (222)	2·710
		(1̄11)	5·421			(3̄17)	2·709
		(111)	4·172			(317)	2·690
½	10·55	4·20 (1̄15)	4·155	½	17·0	2·63 (0.0.12)	2·651
		(115)	3·986			(1̄.1.11)	2·565
2	11·05	4·01 (2̄06)	3·977	½	17·45	2·56 (1.1.11)	2·556
		(008)	3·952			(2̄26)	2·447
		(206)	3·339			(028)	2·445
2	13·2	3·37 (3̄11)	3·334	1	18·2	2·46 (3̄19)	2·443
		(311)	3·100			(226)	2·439
3	14·2	3·13 (020)	3·043				
½	14·55	3·06 (022)	2·992			(1̄.1.13)	2·240
		(400)	2·980			(1.1.13)	2·233
		(1̄19)	2·977	1	20·15	2·23 (5̄11)	2·229
10	14·9	2·99 (3̄15)	2·969			(511)	2·226
		(119)	2·959			(0.2.10)	2·220
		(315)	2·820			(420)	2·153
		(2̄.0.10)	2·809			(4̄22)	2·135
6	15·85	2·81 (404)	2·801	3	21·12	2·13 (422)	2·132
		(2.0.10)	2·793			(2̄.0.14)	2·131
		(404)				(2.0.14)	2·118

I	θ(Cu)	d(meas.)	I	θ(Cu)	d(meas.)	I	θ(Cu)	d(meas.)
1	21·6	2·09	½	27·0	1·693	½	33·95	1·376
2	22·85	1·980	½	27·85	1·645	½	37·25	1·270
½	23·65	1·916	½	28·7	1·601	½	39·1	1·219
1	24·25	1·872	½	29·8	1·547	½	40·0	1·196
½	24·95	1·823	½	31·1	1·488	½	43·6	1·115
2	25·8	1·766	½	31·8	1·459			

group is uniquely determined by the missing reflections, thus establishing the monoclinic prismatic class and excluding orthorhombic symmetry, which is geometrically possible, and triclinic symmetry, which has been suggested in Dana (1944). As shown by old and new goniometric observations, crystals of pyrostilpnite are geometrically "orthorhombic" with indistinguishable (hkl) and ($\bar{h}kl$) forms. It seems best, therefore, to take the equivalent lattice cell which has $a = [201]$, $b = [010]$, $c = [001]$, and the space-group symbol $B2_1/c$. This cell has the following dimensions[1] with which are compared Professor Murdoch's cell dimensions obtained on a crystal from Randsburg (material no. 6):

$$a = 12{\cdot}15,\ b = 15{\cdot}81,\ c = 6{\cdot}23\ \text{kX},\ \beta = 90^\circ\ 00'\ \text{(M. A. P.)}$$

$$a = 12{\cdot}2,\ b = 15{\cdot}87,\ c = 6{\cdot}28\ \text{kX},\ \beta = 90^\circ \pm 30'\ \text{(J. M.)}.$$

[1] In Å. the unit-cell dimensions of pyrostilpnite are $a' = 6{\cdot}84$, $b' = b = 15{\cdot}84$, $c' = c = 6{\cdot}24$ (M. A. P.); $a = 12{\cdot}2_2$, $b = 15{\cdot}90$, $c = 6{\cdot}29$ (J. M.).

The rectangular cell dimensions for the crystal from Příbram give the following geometrical ratios which only roughly resemble the presently accepted elements of Luedecke (1882) when these are appropriately transformed:

$$a : b : c = 0{\cdot}7685 : 1 : 0{\cdot}3941, \beta = 90° 00' \text{ (M. A. P., X-ray)}$$

$$2a : b : 2c = 0{\cdot}7094 : 1 : 0{\cdot}3564, \beta = 90° 00' \text{ (Luedecke).}$$

This unsatisfactory comparison is due to the fact that Luedecke's fundamental angles are those of forms which he denotes as (191) and (191); our subsequent goniometric work shows that these forms are in fact (181) and ($\bar{1}$81) in Luedecke's notation, or (141) and ($\bar{1}$41) in ours. Luedecke's fundamental angles then compare tolerably with the angles calculated on our lattice:

Luedecke.	M. A. P. (calc.)
$oo = (191) : (1\bar{9}1) = 110°11'$*	$ss = (141) : (1\bar{4}1) = 109°02'$
$oo = (191) : (\bar{1}91) = 29\ 46\frac{1}{2}$*	$ss = (141) : (\bar{1}41) = 30\ 43$

Crystals of pyrostilpnite are all small laths or plates flattened on (010) and striated parallel to [10$\bar{1}$] and sometimes also to [101]. The forms other than b(010) are all represented by narrow faces in the zone [001] and the geometrically equivalent zones [10$\bar{1}$] and [101]. The reflections are generally poor and only the smallest crystals are unwarped.

Table IV summarizes two-circle measurements on eleven crystals from Randsburg (material no. 6), by Professor Murdoch, and two

Table IV. Pyrostilpnite: calculated and measured two-circle angles.

	Calculated.		Measured.		
	ϕ	ρ	ϕ	ρ	
b(010)	0°00′	90°00′	0°00′	90°00′	*
k(230)	40 56	90 00	41 16	90 00	(4) J. M.
m(210)	68 59	90 00	70 19	90 00	† J. M.
			69 35	90 00	(6) M. A. P.
p(111)	52 27½	32 53½	52 22	33 08	(2) J. M.
q(121)	33 03	43 14	33 01	43 50	† J. M.
			32 52	43 35	(4) M. A. P.
r(131)	23 27	52 11	25 20	50 18	(1) J. M.
			23 19	52 07	(8) M. A. P.
s(141)	18 01	58 54	18 28	59	(1) J. M.
			18 10	58 37	(1) M. A. P.
t(151)	14 35	63 50½	14 30	64 28	(4) J. M.

* On all crystals.

† On all Murdoch's crystals.

crystals from Andreasberg (material no. 5), shown in figs. 4 and 5, and compares the angles with those calculated from the elements of the rectangular lattice cell. From both sets of measurements a few single

poor readings requiring complex indices have been omitted as insignificant. The comparison shows that the X-ray elements are satisfactory and it establishes the forms listed.

Table V correlates Luedecke's measurements, omitting some redundant angles, with corresponding calculated angles on our elements. In view of the initial error mentioned above it is not surprising that the comparison is generally poor; but the angles do serve to establish the forms $b(010)$, $m(210)$, $s(141)$, $S(\bar{1}41)$, $p(111)$, $d(101)$, $D(\bar{1}01)$ in our notation. The forms (120), (110), (121) do not seem to be well supported, and the forms (100) (no angles) and (001) (not figured) also need confirmation. The following list correlates Luedecke's notation with ours. The forms with letters (J. M. and M. A. P.) are regarded as established, those without letters as uncertain. Since positive and negative forms cannot be distinguished we must assume each observed form (hkl) implies the corresponding form $(\bar{h}kl)$.

J. M. & M. A. P.	$-(100)$	$b(010)$	$-(001)$	$-(120)$	$k(230)$	$-(110)$	$m(210)$
Luedecke	$a(100)$	$b(010)$	$c(001)$	$\delta(140)$	—	$s(120)$	$m(110)$
J. M. & M. A. P.	$d(101)$	$D(\bar{1}01)$	$p(111)$	$P(\bar{1}11)$	$q(121)$	$Q(\bar{1}21)$	$r(131)$
Luedecke	$d(101)$	$d'(\bar{1}01)$	$\pi(121)$	$\pi'(\bar{1}21)$	$p(141)$	$p'(\bar{1}41)$	—
J. M. & M. A. P.	$R(\bar{1}31)$	$s(141)$	$S(\bar{1}41)$	$t(151)$	$T(\bar{1}51)$		
Luedecke	—	$o(191)$ $= (181)$	$o'(\bar{1}91)$ $= (\bar{1}81)$				

TABLE V. Pyrostilpnite: interfacial angles.

	Calculated (M. A. P.).		Measured (Luedecke).	
bm	$= (010) : (210)$	$68°59'$	$= 70°56'$	(8)
			$69\ 13\frac{1}{2}$	(1)
	$(010) : (120)$	$33\ 03$	$b\delta = 36$ca.	(5)
	$(010) : (110)$	$52\ 27\frac{1}{2}$	$bs = 54\ 49$	(5)
bs	$= (010) : (141)$	$35\ 29$	$bo = 35\ 39$	(5)
			$35\ 00$	(1)
bS	$= (010) : (\bar{1}41)$	$35\ 29$	$bo' = 35\ 02$	(1)
bq	$= (010) : (121)$	$54\ 57\frac{1}{2}$	$bp = 57\ 32$	(1)
bp	$= (010) : (111)$	$70\ 40\frac{1}{2}$	$b\pi = 71\ 07$	(1)
dD	$= (101) : (\bar{1}01)$	$54\ 18$	$dd' = 54\ 23$	(1)
cd	$= (001) : (101)$	$27\ 09$	$cd = 26\ 30$	(1)

Despite the generally poor development of pyrostilpnite crystals it is interesting to find a fair agreement between the actual form development and that required by the Bravais–Donnay principle, according to which the importance of a crystal form is proportional to the spacing of the corresponding lattice planes in the notation appropriate to the space group. The lack of a straightforward explanation of this empirical approximation has led to some disbelief in the actuality of the relationship, and therefore another example may not be superfluous. Occa-

onally, as in muscovite (Peacock & Ferguson, 1943, p. 77), there is lmost perfect agreement between the occurrence and statistical im-ortance of the forms of a crystal species and the sequence of lattice lanes in order of decreasing spacings; more often, as in axinite (Peacock, 939, p. 98), the well-established forms tend to appear at the head of the st without close proportionality between form importance and spacing.

Table VI lists the first 34 sets of lattice planes of pyrostilpnite in der of descending spacings, the indices (*hkl*) being in the form appro-

TABLE VI. Pyrostilpnite: theoretical and actual form development.

(*hkl*)	*d* (kX)	Form.	(*hkl*)	*d* (kX)	Form.	(*hkl*)	*d* (kX)	Form
020)	7·91	*b*	(311)	3·32	—	(022)	2·90	—
100)	6·08	?	($\bar{3}$11)	3·32	—	(331)	2·85	—
110)	5·67	*m*	(240)	3·31	?	($\bar{3}$31)	2·85	—
111)	5·23	*p*	(141)	3·22	*s*	(420)	2·84	(*m*)
111)	5·23	*P*	($\bar{1}$41)	3·22	*S*	(250)	2·81	—
220)	4·82	?	(321)	3·12	—	(202)	2·77	*d*
121)	4·54	*q*	($\bar{3}$21)	3·12	—	($\bar{2}$02)	2·77	*D*
121)	4·54	*Q*	(002)	3·12	?	($\bar{1}$51)	2·75	*t*
230)	3·98	*k*	(012)	3·06	—	($\bar{1}$51)	2·75	*T*
040)	3·95	(*b*)	(400)	3·04	(?)	(212)	2·73	—
131)	3·82	*r*	(410)	2·98	—	($\bar{2}$12)	2·73	—
131)	3·82	*R*						

riate to the space-group $B2_1/c$: (*hkl*) only with $h+l$ even; (0*k*0) only ith k even; (*h*0*l*) only with h even and l even. The first 13 places orrespond to known forms (including two which were not well estab-shed goniometrically), with (020) in first place in keeping with the rime importance of *b* as a form and cleavage; and the next 20 places ccount for the 10 remaining forms, including doubtful ones and, of ourse, repetitions such as (*m*)(420) which first appeared as *m*(210). This perhaps an average case, in which the agreement between theoretical nd actual form development is far from perfect, but still quite good nough to lead the morphologist to the correct crystal lattice (axial atios and centring) and often to the correct possible space groups.

Figs. 4 and 5 picture the two measured crystals of pyrostilpnite from ndreasberg, which measure 0·17×0·27 mm. and 0·10×0·28 mm. in ross-section, respectively. The first of these crystals is apparently a ngle individual, with a small attached plate in parallel position, and ne monoclinic symmetry is emphasized by the unequal development of ne forms *r q* as compared to the geometrically equivalent forms *R Q*. he second crystal is a twin group in which the principal parts are best escribed as twinned on the *c*-axis with composition plane *b*. Again

the monoclinic symmetry is shown by the unequal development of geometrically equivalent forms and by the striations on b which follow $[10\bar{1}]$ but not [101]. These appearances speak, of course, for the simplest cell in the lattice ($P2_1/c$), but the rectangular cell is the only practical one since positive and negative forms cannot be distinguished.

Cell contents and density.—The simplest (P) cell with the dimensions a' b' c' β' contains

$$Ag_{12}Sb_4S_{12} = 2[3Ag_2S.Sb_2S_3];$$

the rectangular (b) cell a b c β has twice the volume and cell contents. The calculated density is 5·97, confirming the specific gravity 5·94 measured on 6 mg. by Berman (Dana, 1944, p. 369), who suspected that the value 4·3 (Luedecke) was low.

Optics and twinning.—Flat-lying laths of pyrostilpnite are orange-yellow under the microscope and they mostly fail to extinguish completely in any position of the stage. Occasional very thin tips do extinguish at 8–11° to the c-axis and in rare cases symmetrical extinction about the c-axis is noted in twinned plates. The twin law is best defined as, twin axis [001], composition surface (100) or (010), usually the latter, as in orthoclase. Twinned plates joined on (010) would, of course, give the observed lack of extinction. The orientation noted is $Y = b$[010], $X : c$[001] = 8–11°, as in Dana (1944); the sign could not be definitely determined.

X-ray powder pattern.—The pattern of pyrostilpnite is quite distinct from that of xanthoconite. The numerical data are given in table VII.

TABLE VII. Pyrostilpnite, $3Ag_2S.Sb_2S_3$; Příbram, Bohemia.
X-ray powder pattern.
Monoclinic, $B2_1/c$.
$a = 12{\cdot}15$, $b = 15{\cdot}81$, $c = 6{\cdot}23$ kX; $\beta = 90°\ 00'$; $Z = 4$.

I	θ(Cu)	d(meas.)(hkl)*	d(calc.)	I	θ(Cu)	d(meas.)(hkl)*	d(calc.)
½	5·5	8·02 (020)	7·905	5	18·5	2·42 (260)	2·417
½	7·1	6·22 (200)	6·075			(440)	2·408
½	7·7	5·74 (210)	5·671	½	19·3	2·33 —	—
1	13·4	3·32 (311)	3·320	½	19·8	2·27 (242)	2·270
		(240)	3·313	½	20·7	2·17 (521)	2·176
4	13·8	3·22 (141)	3·218			(402)	2·175
2	14·3	3·11 (321)	3·120	1	21·4	2·11 (270)	2·117
		(002)	3·115	1	21·6	2·09 (422)	2·097
½	14·7	3·05 (012)	3·056			(171)	2·092
		(400)	3·038	½	22·9	1·975 (123)	1·982
½	14·9	2·99 (410)	2·983			(080)	1·976
10	15·7	2·84 (331)	2·854	5	24·0	1·890 (630)	1·890
		(420)	2·835		24·2	1·875 (280)	1·879
½	16·3	2·74 (151)	2·747			(351)	1·867
		(212)	2·730	2	25·0	1·81) (143)	1·818
5	16·9	2·64 (060)	2·635		25·3	1·799 (640)	1·802
		(430)	2·632			(323)	1·799

*($\bar{h}kl$) is not listed since it has the same spacing as (hkl).

Relation of xanthoconite to pyrostilpnite.—The rectangular multiple lattices of the two minerals show the following close metrical similarities:

Xanthoconite.	Pyrostilpnite.
$a = 11{\cdot}97$ kX	$a = 12{\cdot}15$ kX
$b = 6{\cdot}20$	$c = 6{\cdot}23$
$c = 31{\cdot}82$	$2b = 31{\cdot}62$
$\beta = 90°30\frac{1}{2}'$	$\beta = 90°00'$
Space-group $B2_1/c$	Space-group $F2/d$

However, the relation is not a direct analogy, nor can the cell edges be renamed to produce direct correspondence. In xanthoconite the plane of tabular development and cleavage is perpendicular to the symmetry plane; in pyrostilpnite the plane of platy development and cleavage is parallel to the symmetry plane. This indirect relation was already correctly inferred by Miers (1893, p. 215).

Pyrostilpnite provides another example of the frequent situation in which the lattice (simple or multiple) of a crystal with the symmetry of a particular system is metrically indistinguishable from the lattice typical of a system of higher symmetry. It is really not important whether β is a few minutes off 90° or whether the angle will change a few minutes with change of temperature. The fact is that β is practically indistinguishable from 90° and we are obliged to describe a crystal with rectangular axes as monoclinic. I still find this unsatisfactory and most students find it absurd. No doubt we shall continue this usage, recognizing that the crystal systems are symmetry systems and putting up with the present system names where they lead to self-contradiction; but for didactic purposes, and perhaps in the long run for general use, it seems reasonable to suggest a set of names for the symmetry systems which is in line with the international symmetry notation and involves only a few new self-explanatory terms. Such a proposal is made in a more extended discussion now in press (1950). The names and symbols suggested for the symmetry systems, followed by the names of the normal lattice types, are: monogonal (1) (triclinic), digonal (2) (monoclinic), tri-digonal (222) (orthorhombic, rectangular), trigonal (3) (rhombohedral or hexagonal), tetragonal (4) (tetragonal, quadratic), hexagonal (6) (hexagonal), tetra-trigonal 4(3) (cubic).

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The riebeckite-bearing dikes of Shetland

(With Plate III)

By James Phemister

With data on the chemical composition and constitution of riebeckite by C. O. Harvey and P. A. Sabine

Geological Survey and Museum, London.[1]

Introduction.

THE peninsula in which the mainland of Shetland ends north of Ronas Voe and Colla Firth is occupied mainly by the Ronas Hill Granite. This body is intrusive into a metamorphic series consisting of orthogneiss on the north and paragneiss on the north-east, east, and south-east of the peninsula. It is a biotite-granophyre within which earlier bodies of basic rock varying from diorite to gabbro are found. It is unsheared and unfoliated and is cut by a swarm of dikes with north–south trend which extends from the north coast to Ronas Voe. There is evidence also of the existence of dikes earlier than the granite. The later dikes comprise spessartine, microdiorite, porphyrite, quartz-felspar-porphyry, and a great variety of felsites which are generally granophyric and spherulitic. Many of the felsites contain riebeckite and aegirine and have a corresponding blue or blue-green colour. From observation of chilling of dike against dike and intersection of dike by dike it has been found that the basic dikes, spessartine, microdiorite, and porphyrite, are the oldest of the suite, the quartz-felspar-porphyries are older than the felsites, and the blue riebeckite-felsites are younger than white, pink, and dull red felsites which contain neither aegirine nor riebeckite.

The dikes of the swarm range in width from 2 to 30 feet, the only types which exceed the greater width being the quartz-felspar-porphyries which may be 40–45 feet broad. In general the basic dikes are thinner than the acid. Composite dikes are frequent and may include porphyrite, riebeckite-felsite, and riebeckite-free felsite, the riebeckite-bearing member being the latest in all cases.

The sketch-map, fig. 1, shows a large proportion of the acid dikes of the swarm. The basic dikes, omitted for the sake of clarity, outcrop

[1] Communicated by permission of the Director.

over the same area, and are equally numerous as the acid dikes. The riebeckite-bearing members are shown in solid black; the open outcrops include all other varieties of quartz-porphyry and felsite. The map shows that the riebeckite-bearing dikes have a more restricted distribution than the other types. They extend over a lenticular area rather more than 5 miles long and $1\frac{1}{2}$ miles wide at its greatest. They are most numerous, as are the other types, along the north–south median line of the granite and their number falls off rapidly beyond the north and south margins of the granite. They cut the diorite, the granite, and the gneiss, and two of them have been observed cutting the northern contact of the granite and gneiss. It is remarkable that no dikes of any type belonging to the swarm have been mapped east beyond the eastern wall of the granite.

The trend and distribution of density of the dikes show that during cooling the granite had a definite tendency to crack in a north–south direction and that potential cracks were most prolifically engendered along a median zone. The observed contacts of granite with gneiss are sharp and steep; both small and large structures in the gneiss are cut off cleanly and without distortion along the line of contact on the north and east. On the south margin the contact is rarely seen, but at a varying distance from its position a zone of brecciated gneiss cemented by granite is traceable from the Grud Burn eastwards to the mouth of Roer Water and thence northward for fully one mile parallel to the granite contact but separate from it. The intrusion of the granite appears to have been preceded by the development of an arcuate zone of fracture and brecciation, and the rising body of magma punched out a clean plug from the loosened country rock within this zone. There is no evidence that the gneiss was pressed aside during the intrusion and it may be assumed, therefore, that no centripetal pressure was exerted on the granite during its cooling. Contraction on cooling may then have produced actual or potential tensional cracks in a north–south direction parallel to the grain of the country rock, these eventually being opened and filled, in some cases repeatedly, during the final stage of activity, the intrusion of the dikes.

The riebeckite-bearing felsites.

These rocks occur in Shetland only in the small area outlined in fig. 1, but material from them has been found throughout the main island in the shape of stone axes and flensing knives. For such implements the toughness and durability of the rock and its capacity to take

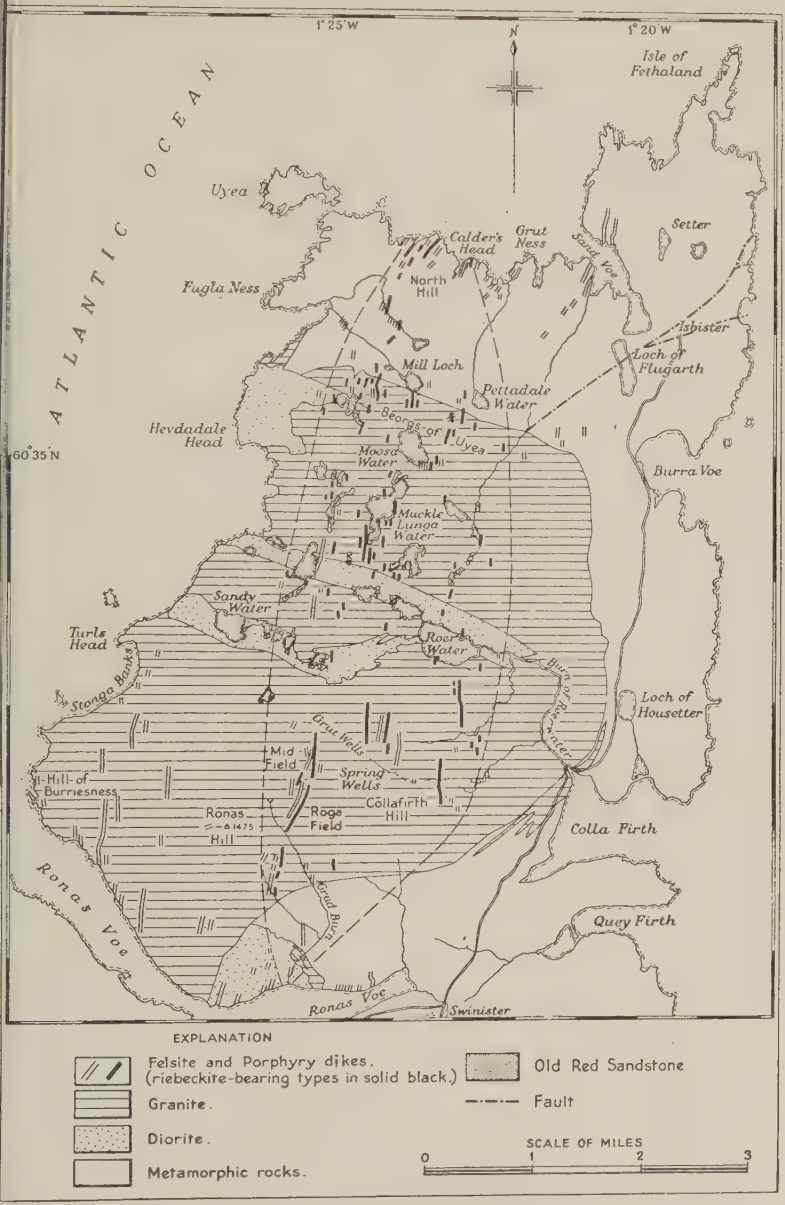

FIG. 1. The acid dikes, granite, and diorite of North Roe, Shetland. (Geological sketch-map, simplified from the manuscript 1-inch Geological Map.)

a clean, sharp edge render it pre-eminently suitable and former inhabitants of the island have evidently been well aware of its source.

The dikes are not quarried and they are so remote from transport that material from them would be expensive. Nevertheless, for special work they might repay working. Their texture and beauty render them admirably suited for curling stones and their colour might be especially effective in small monumental work and in ornamental design.

The riebeckite-bearing rocks are recognized at once by their colour, which is a blue varying in intensity from specimen to specimen according to the proportion and disposition of the riebeckite within the rock. The blue felsites were not observed by Hibbert or by Heddle, the earliest geological students of Shetland, and the first description of them is by Coles Phillips in 1926. His paper describes a dike of porphyritic riebeckite-granophyre, which is unusual in containing epidote, and provides chemical analyses of the dike and of the granite. He notes the similarity of dike and granite with regard both to chemical composition and to granophyric texture and refers both to the Old Red Sandstone period of igneous activity.

The riebeckite-bearing dikes include non-porphyritic homogeneous types ranging in tint from fairly deep blue to dove grey and stone grey, non-porphyritic, spherulitic types in which dark blue spots ranging from 1 mm. to 1 cm. in diameter are conspicuous in a pinkish or stone-grey matrix, and porphyritic, spherulitic types in which pink or red phenocrysts of felspar, clear blebs of quartz, and deep blue spherules combine with a blue-sprinkled silver-grey ground to make an unusual and handsome stone. Variations in the proportion and size of phenocrysts and spherulites, relative to each other and to the groundmass, together with variation in the content of riebeckite, produce a wide range of colour and textural varieties. It is sufficient to describe here the two end-types.

(*a*) *The non-porphyritic, non-spherulitic riebeckite-felsites.*—These rocks are homogeneous and fine-grained, blue, purplish, or pale mauve in colour according as the ferriferous constituent is solely fresh riebeckite or includes less or more limonite. The typical specimen (35303),[1] of which the chemical composition is shown in col. 1 of table I, is composed microscopically of prismatic grains of micropegmatite and granular quartz among which diversely arranged slender prisms of riebeckite are uniformly distributed. Aegirine is usually present but generally in

[1] The numbers in brackets are serial numbers in the Geological Survey collection of Scottish sliced rocks.

subordinate proportion, and occurs mainly as stout subhedral prisms within the quartz pools infilling the mosaic of micropegmatite which is the main component of the rock. This intergrowth of quartz and felspar may be cryptopegmatite in which the two constituent minerals cannot be resolved but are indicated by an appearance of roughness arising from difference in refractive index of the contiguous particles, or it may be quite coarse and in general becomes coarser with distance from the centre of the grain. The micropegmatite has in general a plumose or bushy growth spreading from the centre of the grain, and in this character we find the link which joins this end-type to the spherulitic facies. The quartz of the intergrowth is usually in optical continuity with one of the grains which form the interstitial pools of quartz. The riebeckite prisms reach up to 0·5 mm. in length and are idiomorphic, yielding six-sided basal sections showing the amphibole cleavage and sometimes exhibiting zoning in different depths of colour (pl. III, fig. 2). Aegirine may be almost as abundant as riebeckite, as in specimen 37814, and the optical properties $\alpha = 1{\cdot}768$, $\beta = 1{\cdot}805$ indicate, according to Sabine's diagram (1950) of optical and chemical relationship, a composition of $(Na, K)_{0.96}(Mg, Fe^{+2}, Mn, Ca)_{0.08}(Fe^{+3}, V, Ti, [Al])_{0.96}$. The aegirine is therefore closely comparable with acmite from the Quincy granite-pegmatite and from Kangerdluarsuk (Washington and Merwin, 1927, pp. 239–242 and p. 249). The pyroxene may be almost entirely absent, and it was from a specimen (35303) containing very little aegirine that the riebeckite was separated for analysis. The composition and properties of the separated mineral form the subject of a subsequent section (p. 368).

(*b*) *The porphyritic spherulitic felsites.*—The typical example of these dikes, which has been analysed, col. 2, table I, is a handsome rock (29704) showing in hand specimen pink prisms of felspar, dark clear blebs of quartz, and blue spherulites in a silvery grey groundmass plentifully besprinkled with tiny blue prisms of riebeckite. The phenocrysts and spherulites are of about the same order of size, namely 2 to 3 mm. in length of diameter. Under the microscope the porphyritic quartz and felspar are seen to be idiomorphic though mutually interfering when in cumulophyric aggregates. The quartz crystals are corroded, but not extensively, and the corrosion appears to be contemporaneous with crystallization of the groundmass since the corrosion embayments are not filled by the groundmass as a sack is filled with grain but show ill-defined walls penetrated by crystals of felspar and continuous with quartz granules of the groundmass. The felspar phenocrysts show

twinning according to the Carlsbad and Baveno laws, the optical axial angle is near to 90° and β is 1·523. In appearance the felspar is generally turbid, and may be homogeneous or consist of an intergrowth which resembles microperthite. The two components of the intergrowth cannot, however, be distinguished by difference in refractive index but only by a difference in orientation. The optical properties show that the felspar is a soda-orthoclase, and when the intergrowth is on a fine scale and on a regular plan the crystal has the shot-silk appearance associated with this species of felspar. Rarely the phenocrysts include a water-clear soda-sanidine (37819) with small 2V (pl. III, fig. 4). Some show signs of xenocrystic origin, being replaced by microgranular aggregates of albite, orthoclase, and quartz (37813) and as illustrated by Phillips (1926, pl. viii).

The groundmass of the rock consists of micropegmatite spherulites which crowd upon one another and are cemented by clear granular quartz with which stout hypidiomorphic prisms of alkali-felspar are associated. Riebeckite forms fine needles, rarely intergrown with aegirine, which radiate from the centre of the spherulites and produce the blue spots so conspicuous in hand specimen (pl. III, fig. 3). The blue amphibole occurs equally abundantly as less slender prisms which are arranged diversely, some within the spherulites but most within the areas of granular quartz in association with aegirine. Where these pools of quartz are large the quartz, riebeckite, and aegirine increase in size, and intergrowth of riebeckite and aegirine is frequent, the *c*-axis of the two minerals coinciding and riebeckite being enclosed by aegirine. Alkali-felspar is present also and presents crystal outlines to all the other minerals and is often optically continuous with the felspar of the spherulitic micropegmatite. The mutual relations indicate that quartz was the latest mineral to crystallize and was preceded by aegirine, riebeckite, and felspar in that order.

Between these end-types lie many varieties. Some are non-porphyritic but finely speckled with tiny blue spherulites (37803), some only subspherulitic and with little radiating riebeckite (37818), while in others with good spherulitic structure the riebeckite is entirely in the matrix (cf. pl. III, fig. 5). Fluxional banding is shown by differences in size and abundance of microspherulites (37823) and by fluidal arrangement of riebeckite (37832).

It is noteworthy that the finer the grain of the riebeckite the more intense is the blue colour of the rock (28519, 37823), thus the bluest varieties are often from the chilled marginal portions of the dikes.

Felsites without riebeckite or aegirine.

White, pink, brown, and red felsites occur, as shown in fig. 1, over a much wider area than the riebeckite-bearing dykes. They occur as independent dikes, as dikes juxtaposed to the blue dikes, banded with the blue dikes, or they may themselves have minor blue portions. For example, the dike at the mouth of the Grud Burn at its south end consists of 16 feet of pink felsite in the centre with a blue tint appearing $1\frac{1}{2}$ feet from and deepening towards the margin; at its north end it is $1\frac{1}{2}$ feet wide and the bluish margins are only 4 inches broad.

The majority of the dikes without riebeckite are spherulitic or subspherulitic. The exceptions are the quartz-felspar-porphyries (37846–7), which consist of a fine-grained felsitic groundmass containing no micropegmatite and carrying numerous and large phenocrysts of quartz and felspar, 1–2 cm. long, and sometimes smaller crystals of biotite (37848–9). Some of these porphyries contain much epidote and a little orthite (35143). These dikes are usually broad, reaching 45 feet in width.

There is the same diversity of texture in the pink, brown, and red felsites as in the riebeckite-bearing types. They are composed essentially of micropegmatite and cryptopegmatite which form tables or prisms with a stellate or sheaf-like arrangement or build spherulites. Felspar is common as small skeletal crystals at the centre of such subspherulitic growths and also as small subhedral prisms among the granular quartz which is interstitial to the micropegmatite prisms and is often optically continuous with the quartz of an adjacent micropegmatite individual. The dark mineral of the dikes is usually chlorite which exactly reproduces the various habits of riebeckite. Thus it may occur as ragged needles radiating in the spherulites (35300), or as diversely disposed needles among micropegmatite spherulites (37817, 37857). The chlorite is often studded with minute granules of ore; its acicular form is deceptive and due to a wavy but in general parallel juxtaposition of thin flakes. In some specimens its place is taken by green biotite (37845), and it may be that much of the chlorite is pseudomorphous after biotite. In the analysed rock (29703) the green mineral forms needles, up to $0{\cdot}1 \times 0{\cdot}03$ mm. in size, the outline of which suggests that the mineral is hard and has a high refractive index compared with ordinary chlorites. Birefringence is low, elongation fast, pleochroism Z yellow, X = Y apple green. The properties suggest a mineral of the chloritoid group, but further study is required for identification.

In some dikes chloritized biotite is micro-porphyritic as in the quartz-felspar-porphyries but their association with the others is shown by the

abundance of spherulitic micropegmatite and acicular chlorite (37829). Epidote is often present in the biotitic types (35138).

Among the brown felsites is a 2-foot dike, cutting the granite towards the west end of the Beorgs of Uyea, which exhibits spherulitic structure particularly well (pl. III, fig. 1). A similar dike, in which the spherulites are not so large but have sharp peripheries so that on weathering they fall out as small balls, occurs in the burn south of North Hill.

Composition, classification, and age of the felsites.

Chemical analyses of three of the felsites are given in columns 1, 2, and 3 of table I, in which is quoted also Coles Phillips's analysis of a riebeckite-granophyre from Grut Wells (see fig. 1), another member of the series described in this paper. Analyses of similar or allied Scottish rocks are quoted in cols. B and C. Those of the well-known riebeckite-orthophyre of Holy Island, Arran, and riebeckite-microgranite of Ailsa

TABLE I. Chemical composition of riebeckite-bearing and other felsites.

	1.	2.	A.	3.	B.	C.	D.	E.
SiO_2	76·20	76·13	74·79	75·88	75·20	74·75	73·35	78·02
Al_2O_3	11·03	11·21	10·93	11·19	12·65	12·59	14·38	11·98
Fe_2O_3	1·58	1·66	2·26	2·44	1·53	1·47	1·96	1·45
FeO	1·45	1·45	1·64	1·10	0·28	0·53	0·34	—
MgO	0·12	0·11	0·04	0·15	0·26	0·00	0·09	—
CaO	0·20	0·25	0·53	0·44	0·60	0·37	0·26	0·21
Na_2O	4·90	4·30	4·25	4·04	5·67	4·68	4·33	4·16
K_2O	4·39	4·39	4·79	4·39	4·14	4·95	5·66	3·96
H_2O+	0·14	0·13	0·19	0·12	} 0·12	0·46	—	} 0·33
H_2O-	0·05	0·04	0·27	0·07		0·11	—	
TiO_2	0·24	0·28	0·36	0·31	0·12	0·08	—	—
P_2O_5	0·15	0·17	—	0·00?	—	0·03	—	—
MnO	0·05	0·06	n.d.	0·06	0·10	0·01	—	—
	100·50	100·18	100·05	100·19	100·67	100·03	100·37	100·11

1. Granophyric riebeckite-felsite, non-porphyritic, non-spherulitic type (29707). Beorgs of Uyea, 1,300 ft. 10° S. of W. of the outflow from Mill Loch, North Roe, Shetland. Analysed by B. E. Dixon, Summ. Progr. Geol. Surv. Gt. Brit., 1934, for 1933, Part 1, p. 90.

2. Granophyric riebeckite-felsite, porphyritic spherulitic type (29704). Beorgs of Uyea, 1,000 ft. SW. of outflow from Mill Loch, North Roe, Shetland. Analysed by B. E. Dixon, Summ. Progr. Geol. Surv. Gt. Brit., 1934, for 1933, Part 1, p. 90.

A. Riebeckite-granophyre, Grut Wells, North Roe, Shetland. Analysed by F. Coles Phillips, Geol. Mag., 1926, vol. 63, p. 75.

3. Spherulitic brown felsite, 'eyed' type (29703). Beorgs of Uyea, 1,060 ft. 31° S. of W. of outflow from Mill Loch, North Roe, Shetland. Analysed by B. E. Dixon, Summ. Progr. Geol. Surv. Gt. Brit., 1934, for 1933, Part 1, p. 90.

B. Aegirine-felsite, Cnoc an Droighinn, Assynt, Sutherland. Analysed by W. Pollard; B. N. Peach et al., 'The Geological Structure of the North-west Highlands', Mem. Geol. Surv. Gt. Brit., 1907, p. 449.

C. Quartz-riebeckite-felsite. Dirrington Little Law, Berwickshire. Analysed by J. Jacob; J. Irving, Geol. Mag., 1930, vol. 67, p. 540.

D. Paisanite. Mosquez Cañon, Apache Mts., Texas. Analysed by A. Osann, Tschermak's Min. Petr. Mitt, 1896, vol. 15, p. 439.

E. White material forming small lithophysae in solid black obsidian. Obsidian Cliff, Yellowstone Park, Wyoming. Analysed by S. L. Penfield; J. P. Iddings, 7th Ann. Rep., Director, U.S. Geol. Surv., 1888, p. 282.

Norms of the Shetland micrographic felsites.

	1.	2.	3.
Q	33·18	34·02	35·10
or	26·13	26·13	26·13
ab	31·96	33·01	33·01
ac	4·62	2·77	0·92
ns	0·98	—	—
di	0·26	0·48	0·86
wo	—	—	0·46
hy	2·40	1·73	—
mt	—	0·93	2·78
hm	—	—	0·16
il	0·46	0·61	0·61
ap	0·34	0·34	—
symbol ...	I. 4.1.'4	I. 4.1.3	I. '4.1.3

Craig (Tyrrell, 1928, p. 237) are similar but lower in silica and richer in alkalis. For comparison the analysis of paisanite (col. D) and of the white material forming lithophysae in the spherulitic obsidian of Obsidian Cliff are also shown.

Among themselves the Shetland rocks are almost identical, though the three analysed differ widely in texture and the brown one differs markedly in the mineralogy of the dark minerals. It will be noticed that there is little acmite in its norm and that as compared with the riebeckite-felsites the brown contains more iron and also more alumina though considerably less alkalis. This chemical distinction corresponds with diagnosis of the green mineral in the brown felsite as an iron aluminium silicate resembling chloritoid.

In his description of the dike from Grut Wells, Coles Phillips gave it the name riebeckite-granophyre and this classification is appropriate if the term granophyre is used as defined by Rosenbusch. All the rocks, however, are not porphyritic and it might be better to describe them generally as micrographic riebeckite-felsites.

Age.—The dikes are later than the granite but so closely related areally, structurally, and petrographically to it that they must belong to the same igneous episode. The granite is later than a large fault which courses north-east and is parallel to a fault which lets down Old Red Sandstone conglomerate and sandstones into the schists on the coast east of Setter. The granite may therefore be later than the local Old

Red Sandstone sediments. Finlay (1930, p. 693) accepts the granite as of lower Old Red Sandstone age. He suggests, however, that the riebeckite-felsites are of Tertiary age. Since there are in Scotland riebeckite-bearing lavas or intrusions of Ordovician, Caledonian, and Carboniferous as well as of Tertiary age, no conclusion on the question of age can be reached on the basis of mineralogical similarity.

Composition and constants of riebeckite.

Riebeckite was separated from a specimen (35303) of the non-porphyritic non-spherulitic type in which the amphibole formed prisms averaging 0·1 mm. long and 0·01 mm. broad and in which only a very little aegirine was present. It was necessary to crush the rock to pass the 300 B.S. sieve in order that the amphibole could be obtained without adherent quartz and felspar. Separation was effected by sinking in bromoform. Grain counts on several mounts showed that the impurities were: aegirine 0·02, quartz 0·007, felspar 0·008 %.

Before examination the mineral powder was cleaned successively with chloroform and alcohol and was dried at a temperature of 105° C. After determination of specific gravity, the mineral was again dried at 105° C. and was finally allowed to dry in air. The chemical determinations carried out on the semi-micro scale gave the figures shown in col. I of table II. In the other columns analyses are quoted for riebeckites which are of similar composition and of which some of the optical properties have been determined.

TABLE II. Chemical analyses, optical constants, &c., of riebeckite.

	I.	A.	B.	C.	D.	E.
SiO_2	51·3	51·79	51·94	49·92	46·98	51·01
Al_2O_3... ...	2·7	0·68	0·20	1·99	1·29	0·80
Fe_2O_3... ...	14·2	14·51	18·64	13·35	11·93	16·41
FeO	18·5	21·43	19·39	18·46	23·38	17·62
MgO	n.d.	0·10	1·37	2·07	0·13	0·22
CaO	1·1	1·28	0·19	1·25	1·91	0·19
Na_2O... ...	6·0	6·16	6·07	6·55	8·90	7·98
K_2O	1·4	1·10	0·04	0·95	2·74	1·80
H_2O+ ...	1·9	1·30	2·58	2·03	1·10	0·91
H_2O- ...	0·1	0·10	0·31	0·24	none	
TiO_2	1·9	1·28	—	0·65	1·49	0·96
MnO	0·9	1·15	—	2·24	0·24	0·48
F	0·3	0·20	—	0·45	—	1·70
	100·3	101·08	—	100·15	—	100·64*
Less O for F...	0·1	0·09	—	0·19	—	0·71
Sum	100·2	100·99	100·73	99·96	100·09	99·93

*Includes 0·56 % Li_2O.

α	1·701		1·698		1·691	1·687(?)
β	1·710	1·695	1·699	1·6934	1·694	1·697
γ	1·717	yellow	1·706		1·699	1·703
γ–α	0·016	—	0·008	0·003–4	0·008	—
Sign	—	—	+	—	+	-
2V	? ca. 80°	large	—	large	large	—
c : a	3°–4°	4°–5°	0°	0° (red) 3°–5° (blue)	3°–5°	9°
O.A.P. ...	$\perp$(010)	$\perp$(010)	Z = b	$\perp$(010)	Z = b ?	—
Sp.gr. ...	3·32†	3·391	—	3·371	—	—

† Determined by pyknometer. The value 3·32(5) was obtained also by P. A. Sabine using the method of immersion in heavy liquids. Sabine notes that the powdered mineral displayed some variation on each side of this figure.

I. Riebeckite separated from granophyric riebeckite-felsite (35303). East end of the Beorgs of Uyea, North Roe, Shetland. New analysis by C. O. Harvey.

A. Riebeckite, crystal from pegmatite. Quincy, Mass. Quoted from C. Palache and C. H. Warren, Amer. Journ. Sci., 1911, ser. 4, vol. 31, p. 549.

B. Fine fibrous, blue crocidolite. Kliphius, S. Africa. Analysed by H. E. Vassar; M. A. Peacock, Amer. Min., 1928, vol. 13, p. 256. The optical properties refer to an acicular facies.

C. 'Osannite', from pegmatitic patches in umptekite. Quoted from A. Vendl, Zeits. Krist., 1924, vol. 60, p. 139.

D. Riebeckite, from granite. Mill Mt., New Hampshire. Analysed by F. A. Gonyer; R. W. Chapman and C. R. Williams, Amer. Min., 1935, vol. 20, p. 512.

E. Riebeckite, from granite. South Kigom Hills, Nigeria. Analysed by F. A. Gonyer; R. A. Mackay, R. Greenwood, and J. E. Rockingham, Bull. Geol. Surv. Nigeria, no. 19, 1949, p. 49.

Note on the determination of $H_2O > 105°$ *C.*

Accurate determination of combined water in some minerals is difficult for several reasons (Harvey, 1939). These are mainly concerned with the difficulty of ensuring that the expulsion of combined hydrogen from the mineral and its recovery in the form of water are complete.

Methods in which the temperature is inadequate or which restrict the supply of atmospheric oxygen, for example, the Penfield method, may yield figures for hydroxyl which are smaller than the true value. Internal oxidation of ferrous iron by hydroxyl (the 'basaltic hornblende' reaction, discussed by Hallimond, 1943) may cause some liberation of gaseous hydrogen, which, in the absence of an adequate supply of atmospheric oxygen, may be lost instead of being oxidized to and being weighed as water.

The smallness of the sample of riebeckite did not allow much scope for experimentation, but a figure for $H_2O > 105°$ C. which is believed to be in error by less than $\pm 0·1$ was obtained by a special method. This was a modified semi-micro adaptation of the method described by Harvey (*loc. cit.*, 1939), a platinum-rhodium tube being used and complete con-

version of hydroxyl to free water being facilitated by heating the mineral powder with a flux containing sodium tungstate and potassium permanganate. Other methods also were applied and the figures obtained were as follows:

Semi-micro Penfield method	... ...	1·78 % $H_2O > 105°$ C.
Special method	... ...	1·92 % ,,
Calculated from loss on ignition at 1000° C.		2·16 % ,,

As figures obtained by the Penfield method tend to be low, and as the figure calculated from 'loss on ignition' includes any loss of fluorine and alkalis, the intermediate figure obtained by the special method should be nearest to the correct figure. This figure was accepted and rounded off to 1·9 %.

Unit-cell formula.—The X-ray studies of Warren *et alia* (1930) and work by Berman and Larsen (1931) have provided a general formula for the monoclinic amphiboles which shows the limits of isomorphous replacements. This unit-cell formula may be written:

$$(Ca,Na)_2(Na,K)_{0-1}(Mg,Fe'')_1(Mg,Fe''',Al)_4(Al,Si)_2Si_6O_{22}(O,OH,F)_2.$$

On the basis of 24 (O,OH,F) the unit cell of riebeckite from Shetland contains the following numbers of ions:

Si	7·82	8·00
Al	0·18	
Al	0·32	6·88
Ti	0·22	
Fe''' ...	1·63	
Fe'' ...	2·36	
Mn	0·12	
Na	1·78	
Ca	0·18	
K	0·27	
OH... ...	1·92	2·07
F	0·15	
O	21·93	

The unit cell contains only seven metal atoms and the atoms of the group $(Na,K)_{0-1}$ of the general formula, which are usually assigned to the 'vacant space' of the amphibole structure, are not present in the riebeckite. Little aluminium is associated with silicon in fourfold co-ordination.

The deficiency of 0·12 atoms (7·00—6·88) is unexplained. It is improbable that experimental error can account for more than a minor part of this deficiency. The excess (OH + F) 0·07 may easily be due to experimental errors.

In order to make the similarity to the general formula clearer, some of the Na may be assigned to the Fe'' group of ions and some to the

(Ca,Na) group, K, the largest of the cations present, being unsuitable for inclusion in the Fe group. The distribution of the ions is then as follows:

Si	7·82	8·00	Na	1·55	2·00
Al	0·18		Ca	0·18	
Al	0·32	4·88	K	0·27	
Ti	0·22		OH... ...	1·92	2·07
Fe''' ...	1·63		F	0·15	
Fe'' ...	2·36		O		21·93
Mn	0·12				
Na	0·23				

Optical constants.—Because of the high absorption and considerable dispersion of riebeckite, satisfactory determination of the optical constants of this mineral has always proved difficult. Many chemical analyses have been made, but the corresponding optical data are available in only a few cases. Optical study of the Shetland riebeckite was carried out on mounted thin sections, on the powder separated for analysis, and on a thin section made in the usual way and washed clean of canada balsam. Only on fragments picked from this washed section was it possible to obtain optical values related with certainty to the crystal axes because: (1) the powder consists almost wholly of cleavage plates, and (2) the usual method of recognizing by interference figures grains orientated normal to a principal vibration direction is impracticable owing to the high absorption of grains of a size large enough for tests with the conoscope. By fragmentation of a thin section, however, basal sections of the amphibole needles could be isolated and the two corresponding principal refractive indices determined by immersion in oils. In a thin section, normally about 0·03 mm. thick, the mineral is almost opaque in one direction and certainty of the relative refractive indices of oil and mineral was still found difficult of achievement, but it is believed that the following figures are not greatly in error:

$\alpha = 1{\cdot}701$	$\beta = 1{\cdot}710$	$\gamma = 1{\cdot}717$	(Na light)
indigo blue	brownish yellow	indigo blue	

The direction of greatest refractive index, γ, bisects the acute angle between the cleavages, and that of least refractive index, α, is inclined at about 3 or 4 degrees to the prism axis. Therefore the optic axial plane is normal to (010). Measurement by Berek compensator on a basal section gave γ–β equal to 0·007–0·008. It proved impracticable to measure 2V by the universal stage owing to the difficulty of determining extinction positions. In a prolonged search for an interpretable conoscopic picture only one showing an emergent optic axis was found; the

isogyre was diffuse but distinctly curved, the curvature suggesting a 2V of about 80° and a negative sign.

On comparing the results of this study with previous determinations (table II) it will be seen that the refractive indices and birefringence of the Shetland riebeckite are relatively high. They compare closely, however, with values recorded by Suzuki (1938–39) for crocidolite from a quartz-albite-schist from Hokkaidô, namely

$$n_1 = 1{\cdot}700\text{–}1{\cdot}706, \qquad n_2 = 1{\cdot}712\text{–}1{\cdot}719.$$

It is interesting to find general agreement that the optic axial plane is normal to (010) and that the direction of vibration of the yellow ray lies in (010). The varying determinations of refractive index, birefringence, sign, and the lack of information on the optic axial angle show that in the study of riebeckite there still lies a field of research.

X-ray data.—Powder photographs of the analysed riebeckite (35303) were made by P. A. Sabine, who has provided the data summarized in table III. The intensities of lines on the photograph were measured by means of a microphotometer and are given relative to unit intensity for the strongest line.

TABLE III. Interplanar spacings and intensities of lines observed on an X-ray powder photograph (X 88) taken with Co-$K\alpha$ radiation, wavelength 1·7902 Å., in a 9 cm. camera. Riebeckite, North Roe, Shetland.

d	Intensity	*d*	Intensity	*d*	Intensity
8·42 Å	1·00	2·60 Å	0·06	1·684 Å	0·02
4·51	0·23	2·54	0·06	1·661	0·07
3·34	0·09	2·38	0·03	1·639	0·03
3·27	0·14	2·33	0·05	1·619	0·06
3·13	0·59	2·18	0·09	1·594	0·02
2·81	0·11	2·03	0·04	1·504	0·06
2·72	0·23	1·809	0·07	1·458	0·02

References.

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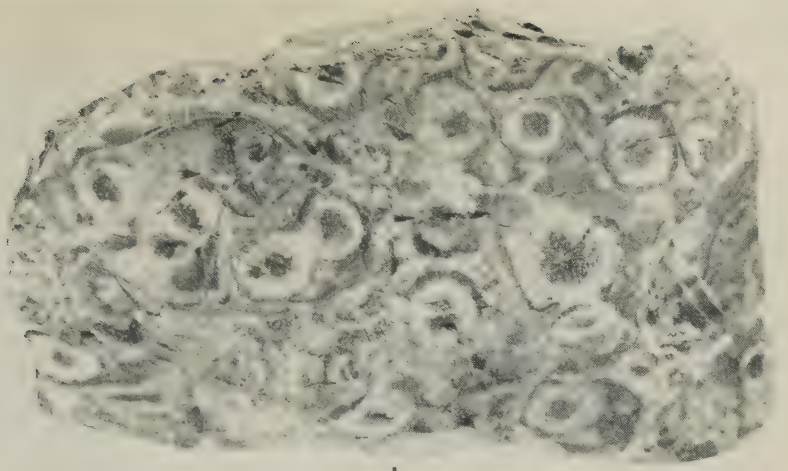

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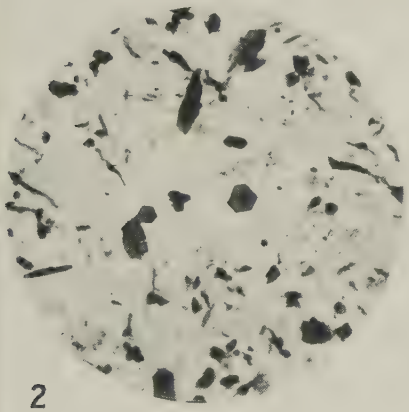

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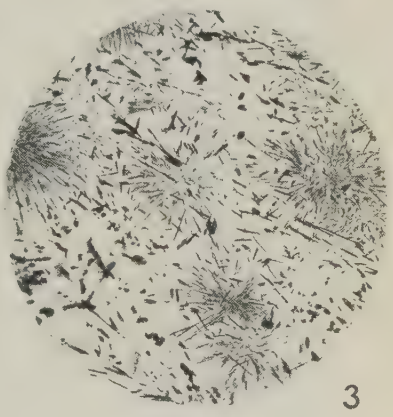

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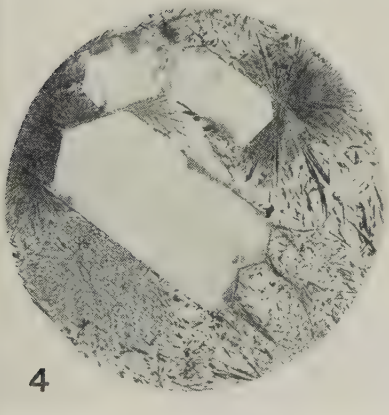

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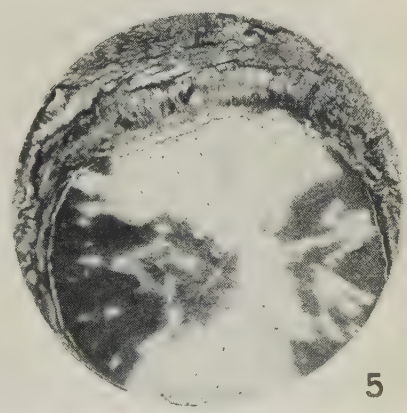

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Explanation of Plate III.

Fig. 1. Spherulitic felsite, brown, 'eyed' type. ($\times \frac{7}{8}$ natural size.) Cf. table I, col. 3.

Fig. 2. Riebeckite-felsite, non-porphyritic, non-spherulitic type. 37810. × 24. Idiomorphic prisms of riebeckite are set in a base of micropegmatite and quartz.

Fig. 3. Riebeckite-felsite, non-porphyritic, spherulitic type. 28515. × 9. Riebeckite radiates as needles along radially spherulitic growths of micropegmatite, and forms stouter prisms in the granular quartz, micropegmatite, and felspar between the spherulites.

Fig. 4. Riebeckite-felsite, porphyritic, spherulitic type. 37819 A. × 10. Spherulitic growths of micropegmatite and riebeckite spread from phenocrysts which project skeletal processes into the spherulites.

Fig. 5. Spherulitic felsite. 28520. × 10. A core of radially arranged cryptopegmatite is surrounded by secondary growths in which riebeckite is concentrated along concentric narrow zones.

Über Josephinit, Awaruit, Souesit, ihre Eigenschaften, Entstehung und Paragenesis

(With Plates IV–VIII)

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(Heidelberg).

I. Einleitung.

In vielen Lehrbüchern der Erzlagerstättenkunde und Mineralogie werden die eigentümlichen Vorkommen von Fe-führendem gediegen Nickel als Musterbeispiele orthomagmatischer Differentiate angesprochen. Daß das bisher, soweit mir bekannt, unwidersprochen geschah, hat verschiedene Gründe:

1) paßt die Durchschnittszusammensetzung Ni_{66} Fe_{33} bis Ni_{75} Fe_{25} leidlich gut mit der Lage des Schmelzpunktsminimums im binären System Ni—Fe
2) stammen die wenigen in situ gefundenen und die recht zahlreichen aus Flußseifen ausgewaschenen Stücke eindeutig aus Serpentinen oder Peridotiten, wodurch ein Vergleich mit den Vorkommen gediegenen Platins in Dunit oder Chromitit nahelag
3) hat das chemisch immerhin unedel Verhalten des Ni und natürlich erst recht des Fe einen Zweifel an der so etwas als *deus ex machina* wirkenden 'orthomagmatischen' Natur garnicht aufkommen lassen und
4) schließlich war das Material in allen Sammlungen so spärlich und wertvoll, daß man sich nicht recht an eine ohne größeren Materialverbrauch nun einmal nicht mögliche Untersuchung getraute und so auch die Zahl der Analysen klein und in der Auswahl des Stoffes — zufälligerweise – - unglücklich war. Es wird im Folgenden erkennbar sein, wie wenig stichhaltig die Gründe 1–3 sind und daß jede etwas umfassendere Untersuchung sofort 'magmatische Ausscheidung' oder gar 'liquides Entmischungsegregat' ausgeschlossen hätte.

Der Verfasser hat, anscheinend erstmalig, vor vielen Jahren (1*a*, *b*) an einer kleinen Schliffprobe einen 'Awaruit' auf dessen erzmikroskopisches Verhalten untersucht und in einem winzigen Fünkchen das schon vor sehr langer Zeit behauptete Vorkommen (2) in Serpentinen der Gegend von Zermatt erzmikroskopisch bestätigen können. Dann hat de Quervain (3*a*, *b*) das verbreitete Auftreten winziger Körnchen von Awaruit in Serpentinen von Selva bei Poschiavo beobachtet und ausführlich beschrieben, Angaben, die dann wieder vom Verfasser (4*a*, *b*) ergänzt

wurden. Das scheint alles zu sein, was erzmikroskopisch über (Ni,Fe)[1] bekannt ist.

Durch glückliche Zufälle wurde dem Verfasser reiches Material von Josephinit zugänglich, das zu mindestens drei verschiedenen Zeiten in den klassischen Vorkommen (Josephine Co., Oregon und zwar besonders Trail Creek Canyon) gewonnen worden war. Zuletzt hat in allerneuester Zeit Herr R. E. Morley (5) in Salem, Oregon, in größerer Zahl kleine erbsen- bis bohnengroße Nuggets auswaschen lassen und dem Verfasser etwa 60 zu Untersuchungen zur Verfügung gestellt, aber weiter fand er in den Sammlungen der Universität Heidelberg zwei Serien desselben Vorkommens in durchschnittlich etwas größeren Stücken vor, die etwa 1896 und 1910 erworben waren. Von ihnen wurden insgesamt 25 Proben angeschliffen. Sodann lagen vor: eine stark bohnengroße Probe von 'Awaruit' von South Fork, California, je ein Körnerpräparat (6 Einzelkörner), Awaruit, von Gorge River, Westland, South Island, New Zealand, und ein solches (etwa 15 Körner), Souesit, von Wheaton Creek, Cassior district, British Columbia, 5 Anschliffe 'Awaruit' aus Selva bei Poschiavo, Schweiz, eine Probe aus vertalktem Serpentin von Gullitzen bei Friesach, Kärnten und schließlich mehrere Anschliffe von Heazlewoodit aus Trial Harbour, Tasmania, welch letztere winzige Fünkchen von (Ni,Fe), hier aber offenbar im Vorkommen und vielleicht im Chemismus von allen früher erwähnten abweichend, enthielten. Die Trial Harbourstücke hat Verfasser neuerdings beschrieben (4*a*); sie werden hier nur eben erwähnt. Allen denen, die dem Verfasser bei seiner Arbeit behilflich waren, durch Bereitstellung von Material, wie durch Hinweise, sei hier herzlichst gedankt. Ich nenne die Herren R. E. Morley, H. Meixner, de Quervain, Campbell-Smith, Claringbull, und Frau Schachner.

II. Erzmikroskopische Beschreibung der Proben vom Josephine Co.

Lange, d.h. seit dem Bekanntwerden des Josephine Co. Vorkommens 1892, ist aufgefallen, daß die kleinen 'Nuggets' keineswegs rein sein können. Beginnen doch die Dichtewerte bei wenig über 4 und gehen meist kaum über 6, bei einem Häufungsmaximum von etwa $5\frac{1}{2}$ (als Ergebnis der Bestimmung an 30 Körnern),[2] während reines Eisennickel

[1] Im Folgenden wird öfter '(Ni,Fe)' abgekürzt, wo das eisenführende natürliche Nickel überhaupt, 'Aw.', 'Jos.', 'Sou', wo die Naturvorkommen mit den eingeführten Namen gemeint sind.

[2] Dass die Schrifttumanalysen an Proben mit Dichtewerte 7·0 und mehr durchgefürt wurden, gibt eigentlich ein ganz falsches Bild der tatsächlichen Verhältnisse! Auch Morley fand als Durchschnitt der Dichtewerte von 15 Stücken 5·66.

ungefähr 8·6 erwarten ließe. Es zeigt sich, daß ganz wechselnde Gehalte an Serpentin, Glimmer (oder/und Chlorit und Talk), Actinolit, Magnetit und Sulfiden das Gewicht unkontrollierbar herabdrücken. Leider ist die Bestimmung der Silikate im Anschliff nur angenähert durchzuführen und die Herstellung von Dünnschliffen nicht möglich.

Die *Analysen*, die zu verschiedenen Zeiten (vergl. z. B. Doelter) zuletzt von R. E. Morley (5) veröffentlicht wurden, streuen in ihren Ergebnissen stark, was nach dem mikroskopischen Befund wirklich nicht erstaunt, da offenbar jeweils Einzelproben, nicht etwa systematisch gezogene Durchschnitte analysiert wurden. Bemerkenswert ist aber ein mehrfach festgestellter Gehalt an Cu (bis 1·2 %), S (bis 0·55 %), und As (0·23) neben der selbstverständlichen Gangart. Auch Co and P werden erwähnt. Spurenelemente, besonders Platinoide, scheinen noch nicht systematisch untersucht zu sein.

Der Mineralbestand ist, soweit es den Erzinhalt betrifft, sehr viel komplizierter, als man es erwarten sollte. Es wurden festgestellt ged. (Ni,Fe) und zwar dieses in zwei öfters nebeneinander vorkommenden Färbungsvarianten, *gediegen Kupfer* und mindestens sieben, vielleicht neun *sulfidische Erze*, ferner *Magnetit* und viele Silikate, besonders Serpentin, Chlorit, Talk, Olivin, Amphibol. Dazu kommen als oberflächliche Neubildungen Limonit, Cuprit, Covellin, Hämatit, ein schwarzes Oxyd und spurenhaft andere.

Eisennickel, (Ni,Fe) ist durch sehr gute Polierfähigkeit und die große Widerstandfähigkeit gegen Anlaufen ausgezeichnet (ein Schliff von South Fork war volle 20 Jahre nach der Herstellung noch völlig blank!). Spaltbarkeit war nirgends sicher erkennbar. Das Reflexionsvermögen ist sehr hoch, aber in Öl doch merklich geringer als das der Edelmetalle, vielleicht 75–80 %. Anisotropie fehlt, doch könne feinste, erst bei gekreuzten Nicols wieder durchschimmernde zupolierte Schleifkratzer ebenso feine Einlagerungen von Silikat in den Skeletten und fiederigen Aggregaten etwas davon vortäuschen. Nicht immer ist das Reflexionsvermögen völlig gleich; mehrfach wurde, ersichtlich etwas älter, eine viel reichlichere Komponente, die in Öl eine Spur heller und mehr gelbweiß und eine spärlichere, jüngere, die im unmittelbaren Kontrast etwas bläulich erscheint, beobachtet.

Die Strukturen und Texturen sollen hier an Hand der Photographien beschrieben werden.

Verhältnismäßig selten ist eine auf den ersten Blick körnige Struktur, wie sie etwa die Pl. IV, Abb. 1 u. 2 zeigen. Die deutlich abgesetzten Korngrenzen können durch Körnerzüge von Magnetit oder Silikat

gekennzeichnet sein. Genaue Untersuchung der leicht tadellos zu erhaltenden Schliffe zeigt aber, daß diese Körner absolut nicht kompakt sind, sondern ein mehr oder minder lockeres Gewebe, einen Filz von Skeletten oder fein moosförmiger Massen darstellen mit völlig wirrer oder nur teilweiser Orientierung der kleinsten Einzelkomponenten. Schon hier drängt sich der Eindruck auf, daß die Körner- oder Ballenstruktur ein jetzt völlig verschwundenes körniges Mineral abbildet. Starke Vergrößerungen derartiger Massen lieferten Bilder wie Pl. IV, Abb. 3 u. 4, fiederige Massen, zum Teil strahlig subparallel, oft tannenbaumförmig verzweigt, manchmal sehr locker, so dass (Ni,Fe) nur wenige Prozent der Fläche neben überwiegenden Silikaten einnimmt, manchmal ziemlich kompakt mit nur wenigen Zwischenräumen. Das letztere kann durchaus primär sein, doch kommen Partien vor, wo am Rand der kleinen Nuggets Silikat ausgelaugt beziehungsweise herausgeschlagen und (Ni,Fe) durch den Flußtransport zusammengehämmert ist.

Sehr eigenartig und dabei häufig sind feine Aderfüllungen von (Ni,Fe), die, oft ausgehend von größeren Massen, offensichtlich Sprüngen im Silikat folgen, dieses durchtrümmern und verkitten (Pl. IV, Abb. 5). Ist einmal älterer Magnetit vorhanden (Chromit, der im Schrifttum mehrfach als Begleiter angegeben ist, habe ich nie beobachtet!), so wird dieser gelegentlich, immerhin seltener, auch durchädert. Solche Formen erfassen besonders die an sich etwas zurücktretenden Fälle, wo die Silikate aus der Phase vor der Serpentinisierung, Olivin, Bronzit, Amphibol noch teilweise erhalten sind.

Kompaktere Metallmassen enthalten häufig in sehr wechselndem Anteil deutlich geregelte Einschlüsse von Schichtgittermineralien (Pl. IV, Abb. 6; Pl. V, Abb. 7), von denen Chlorit und Talk, im Anschliff nicht unterscheidbar, vorkommen. Das Korn des (Ni,Fe) steht ohne Beziehung zu dieser Regelung; noch mehr, an gelegentlichen Porenräumen ragen Kriställchen ungestört in diese hinein. Die Ausscheidung des (Ni,Fe) muss also *nach* der Bildung des Chlorits und dessen Regelung erfolgt sein. Es gibt allerdings einmal Stellen, wo auch (Ni,Fe) ausgewalzt und beansprucht ist; das sind aber wieder nur winzige Partien am Außenrand der Stücke, wo das 'Hämmern' durch Kiesbrocken klar ist.

Daß eine komplexe Bildungsgeschichte vorliegt, zeigt besonders auch Pl. V, Abb. 10, wo von Klüften aus, die mit kompakterem (Ni,Fe) und Magnetit erfüllt sind, idioblastisch völlig porenfrei Kristalle in ein lockeres, sicher älteres Metallmoos hineinwachsen. Auch Zwickel, wo mehrere Korngrenzen zusammenstoßen, enthalten oft gute, scharfe Kristalle.

Am auffallendsten sind traubig rhythmische Massen (Pl. V, Abb. 9), wo Magnetit, der seinerseits aber schon wieder ältere kleine Einschlüsse von (Ni,Fe) enthält, rhythmisch umkrustet ist mit Gangart, der (Ni,Fe), wieder Gangart, Limonit (Goethit), wieder Gangart folgt. Ja mehrfach rhythmische Wiederholung des (Ni,Fe) kommt vor. Das heißt, die Metallausscheidung muß beinahe gleich alt mit der Limonit-bildung gewesen sein. Immerhin, dieser Fall und auch die abgebildete Form, ist selten. Meist ist (Ni,Fe) in enger Beziehung zu Magnetit, der einmal älter, einmal jünger ist. Wechselweise durchädern sich beide, oft ersichtlich in mehreren Generationen.

In zwei Fällen waren die 'Nuggets' in Wahrheit Gerölle von ganz überwiegend Magnetit, gehörten aber trotzdem zur Paragenese, da sie auf zugeheilten Klüften fein eingesprengt neben Magnetit jüngerer Generation (erkennbar an schwach abweichenden Eigenschaften) Körnchen von (Ni,Fe) führten.

Damit ist nun die Vielgestaltigkeit noch längst nicht erschöpft. So kommen Sprünge (in so zähem Material natürlich besonders auffällig!) vor, die teils mit Silikat, teils mit (Ni,Fe) in Fasergipsartigen Formen erfüllt sind, Fälle, wo in Serpentin (Ni,Fe) ganz die Rolle des bei der gewöhnlichen Serpentinisierung entstehenden Magnetits einnimmt, wo weiter relativ kompakte Massen siebartig Silikat enthalten usw., usw.

Genetisch von vielleicht entscheidendem Interesse sind aber Bilder, wie sie vielleicht in einem Viertel der untersuchten Proben gelegentlich zu sehen sind (Pl. V, Abb. 8; Pl. VI, Abb. 11, 12) und die teilweise recht grob, aber bis zu Größen von vielleicht 10 μ herunter feststellbar sind. Hier formt (Ni,Fe) zum Teil allein, zum Teil mit Magnetit in mehr oder minder lockerer Raumerfüllung ein einwandfrei oktaedrisches Lamellenwerk ab. Meist sind die Zwickel leer, einigemale silikaterfüllt, öfters auch enthalten sie (Ni,Fe)-Moos oder komplexe Formen. In Pl. VI, Abb. 12 ist übrigens, im Bilde nicht erkennbar, das zwickelfüllende (Ni,Fe) von der etwas blaueren jüngeren Art. Ganz analoge, vielleicht etwas rohere Formen, bildet auch gelegentlich Magnetit, (Pl. VI, Abb. 13) wobei hier — vielleicht zufällig — die Zwickel immer erfüllt waren, zum Teil mit fein moosförmigem (Ni,Fe), zum Teil mit Silikat. Es kann nach Form, Paragenese und Ausmassen kaum ein Zweifel sein, daß die Strukturen der Pl. V, Abb. 8 und Pl. VI, Abb. 13, auf dasselbe Ausgangsmaterial zurückgehen.

Als letzte Struktur des (Ni,Fe) sei noch Pl. VI, Abb. 14 gezeigt, die ein fein- und ziemlich gleichmäßigkörniges Aggregat zeigt, das neben weit überwiegend (Ni,Fe), gediegen Kupfer, Chalkosin, Sulfid III, und

Magnetit führt. Die Form deutet auf ein Rekristallisat. Daß es ein solches ist, verrät wieder die Verteilung; es ist offenkundig an die äußersten Partien einiger Körner gebunden. Daß die Rekristallisation hier bei ganz niederen Temperaturen erfolgt sein muß, ist auffallend, aber unbestreitbar.

Magnetit ist zum Teil schon besprochen worden. Erzmikroskopisch zeigt er wenig Besonderheiten. Eigentlich stets zeigt er eine gewisse Porigkeit, oft ist er ähnlich moosförmig wie (Ni,Fe). Entmischungen zeigt er nie, auch sonst keine Eigenschaft, die auf höhere Temperaturen hindeutete. Martitbildung ist recht selten, aber gelegentlich in Anfangsstadien recht typisch. Ganz merkwürdig ist, daß manchmal von außen her und zwar besonders dort, wo (Ni,Fe) angrenzt, das Martitnetzwerk sekundär wieder rückgebildet ist, sodaß die Martitlamellen nurmehr auf den Innenteil beschränkt sind. Die Farbe ist, wie übrigens für die seltenen Tieftemperatur-Magnetite typisch, fleckig ein wenig verschieden. Über die überaus wechselvolle, auch im selben Stück auf kürzeste Erstreckung hin verschiedene Altersbeziehung zu (Ni,Fe) wurde schon gesprochen.

Ob Magnetit oder ein Ni-reiches Glied der Spinellfamilie, etwa Trevorit vorliegt, ist erzmikroskopisch und auch röntgenographisch nicht sicher zu unterscheiden. Die sämtlichen Beobachtungen deuten auf Magnetit *ohne* wesentliches Ni!

Kupfer. Nur einige Analysen von (Ni,Fe) weisen kleine Gehalte von Cu nach, über die man bei der alten genetischen Deutung und der bei hoher Temperatur bekanntermaßen unbeschränkten Mischbarkeit von Ni und Cu sich keine Gedanken machte. Umso überraschender war es, in etwa einem Drittel aller Proben ged. Cu zu finden, in 2 von 30 Proben in sehr erheblicher, — im einen Fall sicher 20 % (eher mehr) erreichenden Menge. Es ist im (Ni,Fe) ganz unregelmäßig verteilt (Pl. VII, Abb. 15) oder zeigt mit ihm Anzeichen rhythmischer Fällung. Eine sichere Altersbeziehung besteht nicht; Kupfer ist zwar stets jünger als der älteste Anteil des (Ni,Fe)S, wird aber anderseits immer noch vom jüngsten (Ni,Fe) umhüllt. Eine mögliche Ausnahme bilden winzige, offenbar rezent umgelagerte Flitter im Außenrand der Gerölle, die in aufgeblättertem Chlorit ausgefällt sind und anscheinend schneller als die Hauptmasse anlaufen. Abgesehen von dieser letzten unsicheren Beobachtung besteht aber auch für die Hauptmasse weder in Farbe noch Anlaufen eine Abweichung vom Verhalten gewöhnlichen reinen Kupfers. Photographisch läßt sich Cu neben Ni mit starkem Rotfilter leicht erfassen (Pl. VII, Abb. 15) und Abb. 26 and 27, p. 382.

'Sulfide.' In fast jedem Stück sind, meist in winziger Menge und kleinen Fünkchen, Komponenten vorhanden, die man als Sulfide ansprechen möchte. Da einige Analysen aber auch P und As nachweisen, wäre immerhin möglich, dass unter den im folgenden mit Nummern bezeichneten und nur teilweise und mit Vorbehalt gedeuteten Mineralien sich ein Arsenid oder Phosphid versteckte (etwa II, VII); wohlverstanden liegt aber ein sicherer Hinweis dafür *nicht* vor. Die Bestimmung ist in allen Fällen durch die Überstrahlung des (Ni,Fe), die Kleinheit überhaupt und die dadurch bedingte Unmöglichkeit von Ätzung oder röntgenographischem Nachweis ungemein erschwert. Geordnet sind diese Mineralien nach abnehmendem Reflexionsvermögen.

I. Ist nur in 4 oder 5 Schliffen sicher nachgewiesen, jedenfalls aber wegen der Ähnlichkeit mit (Ni,Fe) oft übersehen. I ist auch bei Ölimmersion im (Ni,Fe) schwer erkennbar, eine Spur dunkler, im Kontrast eine Spur grünlich-gelb und schwach anisotrop. Es bildet rundliche oder unregelmäßig geformte Körner und wird anscheinend von (Ni,Fe) ohne neue Reaktionsprodukte verdrängt. Ich halte diese Komponente für *Heazlewoodit*, Ni_3S_2.

II. Zartrosa in Luft, lichtrosabraun in Öl, deutlich anisotrop, aber kaum reflexionspleochroitisch auch in Öl, ist gelegentlich reichlicher, manchmal die herrschende Sulfidkomponente. Die Formen neigen zu lamellarer Entwicklung, wobei die Lamellen durch Verdrängung eigentümlich regelmäßig ein- oder beidseitig gezähnelt aussehen können, oder auch in Schnüre eckiger Perlen aufgelöst sind. Die Eigenschaften passen zu keinem der nach der Paragenese möglichen Mineralien so richtig; Niccolit ist erheblich stärker anisotrop, Maucherit würde eher passen, zeigt aber keinen Reflexionspleochroismus. Es wurde daran gedacht, daß es die NiAs-Modifikation des *NiS*, bisher im Naturvorkommen noch nicht nachgewiesen, sein könnte. Jedenfalls ist die Ähnlichkeit mit dem Kunstprodukt groß. Allerdings müßte dann eine Erklärung für das Fehlen von Mischbarkeit mit IV, das mit größter Wahrscheinlichkeit Pyrrhotin ist (NiS und FeS bilden nach Alsén (7) bei hoher Temperatur ja unbegrenzt Mischkristalle) gegeben werden. Für NiS spricht sehr, daß es oft mit I vergesellschaftet ist und stellenweise in dieses übergeht.

III*a* ist isotrop, zeigt oft erkennbar nach (111) Spaltbarkeit oder wenigstens rohe, der Verwitterung den Weg weisende Risse, läuft manchmal stark, häufiger schwach an und ist auch sonst in seinen Eigenschaften (Farbe, Härte) auch im selben Stück etwas wechselnd. Sehr oft verdrängt es in allen Stadien IV. Auch dieses Mineral läßt sich mit

keinem bekannten Mineral ohne weiteres vergleichen. Die Härte und das Anlaufen schließen Nickellinneit, die Farbe ein Ni-reicheres Glied der Reihe NiS_2—FeS_2 aus. Auffallend ist, daß dieses Mineral sehr oft zerfallen ist unter Bildung von III*b*, das man ohne weiteres nach den so auffallenden optischen Eigenschaften als *Vallériit* anzusprechen möchte, aber wohl ein Ni-reicher Verwandter von diesem ist. Die letztere Beobachtung deutet für III*a* entweder auf Pentlandit, der aber nicht so leicht anläuft, aber in angewittertem Zustande wohl ausnahmslos zum Teil in Bravoit übergeht, oder — und das scheint mir am wahrscheinlichsten — für einen '*Chalkopyrrhotin-Verwandten*', etwa (Ni,Fe,Cu)S mit Zinkblendegitter. — III*a* steht oft in engen genetischen Beziehungen zu (Ni,Fe), die unten näher behandelt und für die Lösung der Josephinitfrage offenbar besonders wichtig sind (Pl. VII, Abb. 17, 18; Pl. VIII, Abb. 19).

IV ist stark anisotrop und in Öl trotz der Kleinheit der Körner erkennbar pleochroitisch. Die Farbe in Luft ist ein sehr lichtes, in Öl ein entschiedenes Braun; insgesamt ist Farbe und Reflexionsvermögen stumpfer als bei II und III*a*. Meist bildet es winzige rundliche Körnchen von etwa gleichmäßiger Größe, gelegentlich auch Verteilung im (Ni,Fe), die keine Anzeichen unmittelbarer Verdrängung durch dieses zeigen. Demgegenüber stehen größere Partien, die nun fast ausnahmslos von III*a* in allen Verhältnissen korrodiert sind (Pl. VIII, Abb. 21). Oft entstehen dabei Relikte, die genau wie die unmittelbar im (Ni,Fe) liegenden Körner aussehen (Pl. VII, Abb. 16; Pl. VIII, Abb. 20) und den Schluß nahelegen, daß (Ni,Fe) zwar III*a* (und auch III*b*) verdrängt, nicht aber, mindestens häufig nicht, unmittelbar IV. - In allen Eigenschaften stimmt IV, soweit es mit den bisher gebrauchten Untersuchungsmethoden an den kleinen Körnchen feststellbar ist, mit *Pyrrhotin* überein.

Während I insgesamt sicher seltener ist, sind II, III*a* und IV verbreiteter und können wechselweise - wohlverstanden in dem immer kleinen Sulfidanteil! — vorherrschen. Sehr arm an Sulfiden überhaupt sind Stücke, die aus überwiegend feinem Moos von (Ni,Fe) bestehen und keine kompakteren Stellen besitzen. Das ist aber nur eine Regel; gelegentlich führen auch die 'Moose' einmal grössere Sulfidkörner (Pl. VIII, Abb. 20). - Diesen erstgenannten gegenüber sind V–IX erheblich seltener und meist auf die Proben mit gediegen Kupfer beschränkt.

V ist ledergrauoliv, stark anisotrop und sehr merklich pleochroitisch, besonders in Öl. Es bildet relativ große Nester von groben Körnern und grenzt oft unmittelbar an gediegen Cu an, von dem es auch offenkundig

verdrängt wird. (Abb. 26, 27.) Es ist wohl unzweifelhaft die Hauptquelle des Cu.

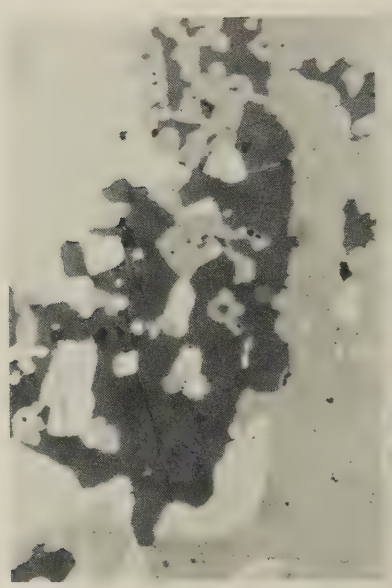

Abb. 26.

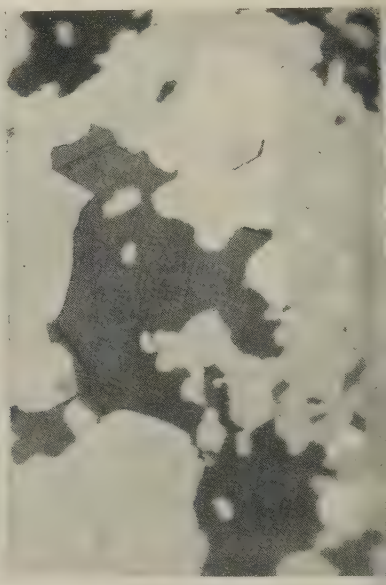

Abb. 27.

Abb. 26. Josephinit, sehr reich an Cu. Kupfer (reinweiß) mit (Ni, Fe) (grauweiß) und reichlich V, das hier von Cu und (Ni, Fe) nicht ersichtlich verdrängt wird. Vergr. 225×, Ölimmersion, starkes Rotfilter.

Abb. 27. Ähnlich Abb. 24. Es ist erkennbar, dass Kupfer offenbar besonders den Raum von zerstörtem V einnimmt. Vergrößerung 600×, Ölimmersion, starkes Rotfilter.

VI ähnelt stark III, ist ebenfalls isotrop, hat aber einen mehr gelblichen Ton und scheint gewisse Verwandtschaft mit Kupferkies zu haben, ist aber, auch bei Berücksichtigung der Überstrahlung durch (Ni,Fe) matter und olivstichig. Da es lokal von IX (Chalkosin) und auch Cu verdrängt wird (Pl. VIII, Abb. 22), steht sein Cu-Gehalt außer Zweifel. Für reinen Chalkopyrrhotin (Cu,Fe)S ist es aber zu gelb. Insgesamt kommt es nur höchst spärlich und selten vor. In einigen Fällen enthält es entmischungskörperartig ein Netz von VIII.

VII und VIII. VII ist erheblich dunkler als V und VI und ähnelt in der Farbe stark VIII. Diesem gegenüber behält es aber die Farbe, während VIII stark nachdunkelt, ohne aber in kurzer Zeit richtig 'anzulaufen' (tarnish by air etching). Außerdem, und das ist der sofort auffallende Unterschied wird VII durch V und stellenweise VI ver-

drängt, während VIII seinersits als Verdränger von beiden auftritt (Pl. VIII, Abb. 22). Beide sind dunkel braunoliv bei frischer Politur, VIII bald schokoladenbraun, wie bei einigen angelaufenen Borniten aus Kunstprodukten (mattes). In VII wurde Anisotropie nicht beobachtet, VIII ist stark anisotrop und wohl hexagonal. Besonders VIII

Abb. 28.

Große Partie von IX ('(Neo)-Digenit'), am Rande zum Teil mit dünnen Filmen von Chalkosin (etwas heller), wird durchädert und verdrängt vom (Ni,Fe). Vergr. 175×, Ölimmersion.

muß wieder einen erheblichen Cu-Gehalt besitzen (Beziehung zu V, Verdrängung durch Cu). — Während V–VIII sich nicht mit Sicherheit mit bekannten Sulfiden von Cu,Ni,Fe identifizieren lassen und V und VIII mit größter Wahrscheinlichkeit neu sein mögen, ist

IX, das nur in einer, der Cu-reichsten Probe überhaupt gefunden wurde, hier aber reichlich und zum Teil in größeren Partien vorhanden ist, mit großer Wahrscheinlichkeit als (*Neo-*)*Digenit* anzusprechen (Abb. 28). Er fällt durch geringe Härte, bläulich fahle Reflexfarbe, Isotropie und dadurch auf, daß er in einigen Fällen, in der Abbildung an Rändern und Sprüngen gelegentlich erkennbar, typisch Umbildung in Chalkosin zeigt. Auch er ist oft von Cu verdrängt, lokal aber auch, wie in Abb. 28,

durch (Ni,Fe). Seinerseits verdrängt er gelegentlich VI, erscheint aber sonst 'primär'.

Junge Oxydationsprodukte haben natürlich nur untergeordnetes Interesse.

Limonit, und zwar fast ausschließlich Goethit, wurde in sehr vielen Stücken, insgesamt aber doch sehr untergeordnet beobachtet. Gelegentlich ist es vergesellschaftet mit dünnen, zum Teil rhythmischen Krusten einer ähnlich reflektierenden, aber völlig opaken Substanz die nicht bestimmbar war; vielleicht war sie asbolanartig. *Cupri* ist aus Kupfer in der Nähe der Gerölloberfläche oder an den Rissen häufig entstanden und an seinen auffallenden Eigenschaften sofort erkennbar.

Die in manchen Analysen nachgewiesenen Elemente Co, As, P lassen sich, wie gesagt, nicht mit Sicherheit auf eines der beobachteten Mineralien zurückführen. Proben von Gullitzen führen Niccolit, der aber wegen seiner auffälligen Eigenschaften hier kaum übersehen wäre, war bei Maucherit immerhin denkbar sein könnte.

Erklärung der Strukturen und des Bildungsvorganges.

Es sei auch hier von der Beobachtung ausgegangen und dazu das bei den Einzelbeobachtungen der Komponenten gesagte ergänzt. Manchmal (Pl. VIII, Abb. 24) finden sich Formen, bei denen ein Netzwerk oktaedrisch angeordneter (Ni,Fe)-Lamellen vorliegt, die gelegentlich in sich wieder komplex aufgebaut sind; ganz innen als Jüngstes ein feines Band von (Ni,Fe), ein ebenfalls schmales von Magnetit an beiden Seiten, dann ein breiteres von (Ni,Fe). Die Zwickel, deren relative Ausdehung in weiten Grenzen schwankt, können mit Silikat erfüllt oder auch leer sein. Selten findet man aber auch (Pl. VIII, Abb. 23) hier kleine Verdrängungsrelikte von III, dessen oktaedrische Risse mit der Anordnung des Netzwerkes der Lamellen übereinstimmen. Mit anderen Worten: Die großen Pseudomorphosen in Pl. VIII, Abb. 24, aber auch die reliktfreien in Pl. V, Abb. 8; Pl. VI, Abb. 11, 12 und vielleicht auch von Pl. VI, Abb. 13 gehen auf III zurück, das ursprünglich in ziemlich großen einheitlichen körnern vorgelegen hat! Besonders instruktiv ist auch Pl. VIII, Abb. 25, wo (Ni,Fe) in jüngerer Verdrängung Magnetit- und Gangartmassen ersetzt, die beide zusammen an der Stelle *eines* alten großen Kornes von wohl ebenfalls III liegen. Das ist erkennbar an winzigen Entmischungskörpern, die nicht an der Verdrängung teilhatten und in Gangart und Magnetit dieselbe Orientierung besitzen.

Damit rundet sich nun das Bild, das sich bei aller Vielgestaltigkeit doch einigermaßen einheitlich darstellen läßt:

Die Bildung von (Ni,Fe) und auch das Cu sind das Produkt eines fortlaufenden Prozesses irgendwie gearteter Umbildung und Oxydation von Sulfiden, verknüpft mit einem zunehmenden 'Edlerwerden' der Produkte. Dieser Vorgang geht bis zur Entstehung der gediegenen Metalle Ni und Cu, während als Oxyd nur das noch sauerstoffarme des Eisens, Magnetit, entsteht, weiter aber erst als oberflächliche rezente Bildung. Vorauszusetzen sind offenbar Sulfide von Fe und Ni, untergeordnet auch Cu. Es waren wohl überwiegend zuerst IV (wohl Pyrrhotin), und III, wobei von diesen ein vermutlich kleinerer Teil erst aus IV umgebildet ist, der Hauptteil aber bereits ursprünglich in großen Körnern vorlag. Aus III geht teils unmittelbar, teils auf dem Weg über die immer Ni-reichen Glieder II und I das (Ni,Fe) hervor. Ein analoger Weg führt von VI über VIII direkt zum gediegenen Cu; in seltenen Fällen entstammt dieses auch dem Digenit, dessen Stellung in der Altersfolge der Sulfide aber sonst unklar ist.

Versuch der genetischen Einreihung.

Welcher Art ist nun aber der umbildende Vorgang?! Der Befund zeigt bei den hauptsächlich untersuchten Josephiniten eindeutig, daß Hoch- oder gar Höchsttemperaturbildung völlig ausgeschlossen ist. Das zeigen allein die überaus wechselnden Strukturen, das manchmal enorm feine Korn, die Moosformen, besonders aber das relative Alter gegenüber der Serpentinmineralien, die rhythmische Fällung von (Ni,Fe) mit gediegenem Kupfer und überhaupt sein Nebeneinandervorkommen mit ihm, die Pseudomorphosen, die wechselnde Altersbeziehung zu Magnetit und so weiter. In den übrigen untersuchten Vorkommen liegen allem Anschein nach völlig analoge Beziehungen vor, insbesondere ist die chemische Übereinstimmung so überraschend, daß man für sie, wie auch alle natürlichen Eisennickel mit 70–75 % Ni (zum Beispiel Piemont, Bobrowka, Yukon) dieselbe Erklärung wird suchen müssen.

Gemessen an der so enormen Verbreitung Ni-haltiger Serpentine ist (Ni,Fe) doch sehr selten und das Verhalten von Ni,Fe und Cu schon so unedel, daß man an sehr ungewöhnliche Bildungsvorgänge denken könnte. Immerhim müßten diese an mindestens fünf Stellen unserer Erdoberfläche, von denen einige schon sehr ausgedehnt sind (ganze Lagerstättenprovinzen wie Alpen, Oregon), realisiert gewesen sein, was wieder ganz 'ausgefallene' Umstände ausschließt.

Die Art der Verwachsung mit Sulfiden zeigt, daß diese bei der Bildung

des Metalls wirksam gewesen sind. Das Vorhandensein oder Fehlen von *Kupfer* in den Stücken desselben Vorkommens und sein offensichtliches Gebundensein an gewisse Sulfide (V–IX) deutet auf geringe Wanderung. Dasselbe zeigen Verdrängungsstrukturen, wo die Kompaktheit des (Ni,Fe) klar von der Art des eingeschlossenen Sulfids abhängt. (Pl. VII, Abb. 17; Pl. VIII, Abb. 20) Das schließt also doch wohl eine Konzentration durch sehr langsame Ausfällung schwach konzentrierter Cu- oder Ni-führender Lösungen aus, oder weist ihnen mindestens eine Nebenrolle zu.

Für viele, meist sehr kleine und Ni-freie Vorkommen von tellurischem Eisen ist die *reduzierende Einwirkung von Sumpfwässern* etwa unter Mooren oder Braunkohlenflözen zur genetischen Deutung herangezogen worden. Das trifft wohl in manchen Fällen sicher zu; auch für das Vorkommen von Cu ist es in Einzelfällen bewiesen. Hier liegt aber das gegenüber Eisen edlere Nickel und Kupfer vor. Ihre Ausfällung aus oxydisch ionisierten Lösungen (Sulfat, Karbonat) wäre also durchaus im Bereich der Möglichkeit. Auch das Auftreten von Magnetit in wechselnder Altersbeziehung zu den Metallen würde recht gut zu diesem Bilde passen, kann doch aus $Fe(OH)_2$ bereits bei Zimmertemperatur Fe_3O_4 entstehen. Eine Abfolge, wie sie in den Pl. V, Abb. 9; Pl. VIII, Abb. 22 ersichtlich ist, wäre dann ohne weiteres verständlich.

In der Tat hat der Verfasser zeitweise an eine solche Lösung geglaubt. Es bestehen aber ganz schwerwiegende und wahrscheinlich diese Deutung völlig ausschließende Bedenken. Höchstens ein gelegentliches Weiterwachsen am Außenrand in traubigen Formen (etwa Pl. V, Abb. 9) könnte so möglich bleiben. Die Vorkommen sind heute ja nicht mehr auf Alluvionen beschränkt, sondern in einer ganzen Zahl von Fällen aus anstehendem Gestein, zum Teil aus tiefen Steinbrüchen oder jugendlich tief erodierten Gebieten bekannt. Das würde eine ganz unwahrscheinlich tiefreichende Einwirkung der reduzierenden Wässer voraussetzen. Dazu kommt nun aber noch die geographisch und, was hier entscheidend ist, die klimatische Verbreitung. Daß zufällig klimabedingte reduzierende Agentien auf dem Gipfel des Riffelhorns, dem Tal von Poschiavo, den fast vegetationslosen Serpentingebieten von Oregon, den Sumpfwäldern des Urals oder des südlichen New Zealand u.s.w. gerade gleichartig wirksam wären, ist natürlich ausgeschlossen!

Es bleibt als Erklärung nur eine *thermale Bildung*. Wirksam waren vielleicht die nur wenig über 100° warmen Wässer, die bei der Serpentinisierung oder eher noch bei deren Abklingen während und nach der Vertalkung wirksam waren (Gullitzen bei Friesach ist eine Talkgrube,

manche Josephinite enthalten sicher beinahe gleichalterigen Talk!). Voraussetzung ist aber weiter die Anwesenheit von reichlich Sulfiden, die entweder selbst Ni-reich oder in der Lage sind, Ni, das bei Serpentinisierung aus Olivin beweglich wird, auszufällen. Vielleicht sind diese beiden Möglichkeiten nebeneinander wirksam, das Hauptgewicht wird aber auf der ersten liegen. Die Sulfide enthalten aber ursprünglich viel, wahrscheinlich stark überwiegend Eisen jedenfalls in ihrem ältesten Anteil; das beweisen das Vorhandensein von Pyrrhotin (IV) und dessen Verdrängung durch III, die Neubildung von viel Magnetit und schließlich auch der Fe-Gehalt im (Ni,Fe). Wie kommt es nun, daß allemal ein Mischkristall Ni,Fe ausgefällt wird, der etwa die Zusammensetzung 3 : 1 bis 5 : 2 besitzt?! Bei dem sicher bereits im selben Vorkommen, erst recht noch in verschiedenen stark schwankenden Verhältnis von Ni und Fe in den Sulfiden ist das sehr auffällig. Offenbar stellt sich ein für die betreffenden Bildungsbedingungen, das heißt für die Temperatur der Talkbildung charakteristisches Ausfällungsgewicht ein, vergleichbar vielleicht mit elektrolytischen Niederschlägen, wo bei gewissen Stromdichten Ausfällungsprodukte etwa gleichbleibender Zusammensetzung entstehen, ziemlich unabhängig davon, wie das Verhältnis der beteiligten Metalle in der Lösung war.

Erkennbar abweichende Zusammensetzung im Verhältnis Ni : Fe macht sich in den vorliegenden Stücken in den erwähnten (S. 376.) seltenen Fällen bemerkbar, wo die jüngsten Teile und einige Zwickelfüllungen deutlich abgesetzt etwas mehr bläulich erscheinen. Das würde dann erheblich geänderten Ausfällungsbedingungen, das heißt absinkender Temperatur entsprechen und vorzüglich in den Gedankengang passen.

Für Kupfer gilt sinngemäß dasselbe. Hier ist bei der Unbestimmbarkeit von V–VIII keine Aussage darüber zu machen, ob analog dem Fe-Ni-Sulfiden eine Anreicherungstendenz für Cu bereits in den Sulfidverdrängungen besteht; wahrscheinlich ist es natürlich mindestens in der Beziehung von Cu : Fe.

Über die *Altersstellung der primären Sulfide* in der Gesamtparagenese ist keine sichere Angabe zu machen. Viele Eigenschaften, zum Beispiel die 'Valleriit'-Ausscheidung, das Auftreten von Entmischungskörpern (Pl. VIII, Abb. 25), einige hier nur zu streifende Verwachsungsformen deuten entschieden auf recht hohe Temperaturen, andererseits sind nie Druckspuren in den Sulfiden beobachtet, die man auf Beanspruchung bei der Serpentinisierung ja erwarten könnte, auch würde, vorausgesetzt daß II wirklich NiS ist, das Nebeneinander von NiS und FeS, selbst wenn es eigentlich ein Nacheinander ist, für niedrige Temperaturen

sprechen. Zwei entscheidende Fragen sind in dem ganzen Komplex noch offen und müssen späteren Untersuchungen überlassen bleiben: Können die an 'Chalkopyrrhotin'-ähnlichen Mischkristallen (Cu,Fe)S gemachten Erfahrungen über Zerfall unter Valeriitbildung und die daraus möglichen Schlüsse auf die Temperaturen auch benutzt werden, wenn Ausgangs- und Umbildungsprodukte reich an Ni sind? Die Haltbarkeit von 'Chalkopyrrhotin' in manchen Nickelpyrrhotinen spricht in gewissem Grade dagegen. Demgegenüber: besteht die Mischbarkeit von NiS und FeS, beide in der NiAs-Modifikation, nicht nur bei solch extrem hohen Temperaturen, wie sie Alsén (7) anwendete? Die erheblichen Unterschiede der Gitterkonstanten ($a_0 = 3{\cdot}42$, $c_0 = 5{\cdot}30$ Å. bei NiS, $a_0 = 3{\cdot}43$, $c_0 = 5{\cdot}79$ Å. bie FeS) scheinen auch hier dagegen zu sprechen.

Insgesamt neigt der Verfasser zur Ansicht, daß Sulfide bereits vor der Serpentinisierung vorhanden waren, daß aber bei dieser und noch später erhebliche Umlagerungen stattfanden, sodaß der jetzt noch verbleibende Bestand vielleicht nirgends dem ursprünglichem entspricht. Im Gegensatz zu Trial Harbour, Tasmania (4) aber, wo der Sulfidinhalt neben Schwefel auch zunehmend reicher an Eisen wird, ist hier eine konstante Anreicherung an Nickel. Vielleicht deswegen, weil dort ein sehr hoch hydrothermaler, hier ein letzten Endes tieftemperierter lateralsekretionärer Vorgang besteht.

Beobachtungen an Eisennickel anderer Herkunft.

Wie schon eingangs gesagt, ist hier die Zahl der Proben oder — wie im Falle Poschiavo — die Größe der Körner so gering, daß wenig Neubeobachtungen gegenüber Josephine County zu erwarten sind. Es sei schon hier betont, daß fast nichts festgestellt wurde, was von dem dort Erarbeiteten abweicht.

Die Proben von *Awarua* sind — wie das auch den Schrifttumsangaben entspricht — meist nur winzig. Massen mit höherem Silikatanteil würden sich bei dieser Größe kaum konzentrieren lassen, außerdem ist die Möglichkeit der Zertrümmerung und Weglösung des Silikats größer. Es erstaunt also nicht, wenn die Proben überwiegend kompaktes (Ni,Fe) enthalten. Es wurden sicher das isotrope III, genau wie oft in den Josephine-Stücken mit einem feinen Sprung von (Ni,Fe) abgesetzt, sobald die ersten Anzeichen von Zersetzung bestehen, und das deutlich anisotrope IV festgestellt. Das letztere besitzt hier eigentümliche Schlauchformen, die auch wieder darauf hindeuten, daß IV nicht unmittelbar von (Ni,Fe) verdrängt wird.

Fraser Co. (Souesit) ist meist noch feinkörniger. Nur in einem Körnchen von (Ni,Fe) wurde ein relativ großes, leicht zu übersehendes Korn von I (Heazlewoodit) aufgefunden. Hier ist der einzige Fall, wo (Ni,Fe) einmal einen Einschluß von idiomorphem Chromit enthält. Vergleiche die Analyse bei Johnston (6).

'Talkgrube Gullitzen'[1] bei Friesach, Kärnten. Die Probe, die eine große Zahl metallisch reflectierender Körnchen enthält, ähnelt weitgehend einigen Stücken von Poschiavo. Die Körner sind teils völlig xenomorph, teils scharf idiomorph (scheinbare Würfel) und dann meist größer. Letztere haben auch einen gelblichen Stich und sind anisotrop. Einmal ist das idiomorphe Material von xenomorphen umwachsen. Offenbar ist das weitgehend analog den Umwachsungen von idiomorphem Heazlewoodit durch (Ni,Fe) von Poschiavo.

Über das Vorkommen von *Selva bei Poschiavo* sei auf die sehr ausführliche Beschreibung durch de Quervain (3*a*,*b*) und die Bemerkungen des Verfassers (4) hingewiesen.

South Fork, Smith River, Californien, das heute nach freundlicher Mitteilung von Mr. Morley kein Material mehr liefert, ist den Oregonstücken so weitgehend ähnlich,[2] daß man auf praktisch übereinstimmende Verhältnisse schließen muß. (Ni,Fe) ist teils kompakt, teils krustenförmig, teils myrmekit- oder skelettartig. An Sulfiden ist III und IV vorhanden; III verdrängt IV in typischer Weise.

Kurze Bemerkungen über terrestrische Eisen- und Eisennickelvorkommen.

Eine gründlichere Durchsicht des zum Teil schon lange zurückliegenden Schrifttums über gediegenes Eisen zeigt, daß geochemisch ein Komplex vorliegt, der bisher nicht ausreichend unterteilt ist. Bei Doelter's Handbuch finden sich Ansätze, die dann aber nicht weitergeführt sind. Jedenfalls ist es irreführend, wenn man die von Ovifak oder vom Bühl bei Kassel bekannten Vorkommen gewissermaßen als Musterbeispiele ansieht; sie sind nur Repräsentanten einer von mindestens 4 recht verschiedenen Gruppen.

1) Die eben erwähnten allein sind Reduktionsprodukte hervorgegangen durch magmatische Wirkung aus Einschlüssen von Fe-Erzen

[1] Nach freundlicher Mitteilung von Herrn Kollegen Meixner wäre an Ort und Stelle die Bezeichnung 'Grießerhof bei Hirt' verständlicher.

[2] Übrigens ist auffallend, daß für dieses Vorkommen im Schrifttum (9) nur feine, selten 1 mm. erreichende Körnchen angegeben werden. Sollte die an sich von einer sehr seriösen Firma vor 40 Jahren gekaufte, etwa 2·5 cm. große Probe doch nicht vielleicht von Josephine County stammen?

mit ebenfalls vom Magma aufgenommenen Kohlen oder vielleicht daraus mobilisierten Kohlenwasserstoffen. Sie sind hauptsächlich aus Basalten bekannt — keineswegs nur von Bühl und Ovifak —, aber auch aus Trachyt, Quarzporphyr und, was bei dessen niedriger Intrusionstemperatur erstaunt, Granit. Sie enthalten Fe, daneben sehr viel Cementit, reichlich Nickel, falls das umgebende Gestein solches enthält und die Einwirkungszeit hinreichend lang war, aber anscheinend keine Platinoide.

Als Anhang zu 1) wären vielleicht zu erwähnen Produkte natürlicher Erdbrände, wie sie z.B. von la Bouche bei Nery, Dept. de l'Allier beschrieben sind und zur Zeit in einem ausgedehnten Vorkommen durch G. Baker aus Australien bearbeitet werden.

2) Eine zahlenmäßig viel verbreitetere Gruppe stellen Fälle dar, wo bei niedriger Temperatur lokal ganz stark reduzierende Bedingungen Eisen metallisch ausfällten. Oft scheinen dabei sich oxydierende Sulfide neben den reduzierenden Kohlenwasserstoffen, also eine Art von Wechselwirkung von Oxydation und Reduktion, wesentlich gewesen zu sein. Es mag etwa ein Dutzend unbezweifelbarer Fundorte hierher gehören, dazu ein paar zu Unrecht diskreditierte. Sie führen keinen als Graphit oder Cementit vorliegenden Kohlenstoff, sehr wenig Ni oder Co (letzteres vielleicht eher mehr), in einem Fall Pt. In allen Fällen überwiegt Fe ganz stark.

3) Nur in wenigen Stücken bekannt, aber durch das Vorkommen von Santa Catharina wohl als terrestrisch gesichert, sind Fälle, wo das Verhältnis Fe : Ni etwa 2 : 1 ist, die also wie der Taenit etwa 33–34 % Ni, sonst aber fast nur Fe enthalten. Über den ursprünglichen geologischen Verband ist praktisch nichts bekannt.

4) Die letzte Gruppe würde das in vorliegender Arbeit Besprochene enthalten. Einige wenige Vorkommen lassen sich, wie zum Beispiel das merkwürdige Eisen von Oktibbeha County, Mississippi, nicht in das vorliegende Schema einordnen.

Am Schluß seien ein Paar gekürzte, das Gesagte unterstreichende Analysen dieser einzelnen Gruppen gegeben. (S. 319.)

Summary.

The occurrences of native nickel-iron regarded as magmatic secretions from peridotites (awaruite, josephinite, souesite, &c.) are certainly formations of extremely low temperatures. This conclusion is drawn from studies of structure and paragenesis carried out principally on a considerable number of josephinites. Nickel-iron (Ni,Fe) is found

Analysen	1		2					
zu:	*a*	*b*	*a*	*b*	*c*	*d*	*e*	*f*
Fe	93·87	93·16	97·79	—	—	99·39	97–10	98·93
Ni ...	—	2·01	0·11	—	2·0	—	—	0·61
C ...	3·20	2·34	—	—	—	—	—	0·79
Co ...	—	0·80	0·23	—	—	-	—	—
Mn ...	0·66	—	0·57	-	—	—	—	—
Cu ...	—	0·12	0·10	-	—	—	-	—
Pt	—	—	—	0·10	-	—	—	-

Analysen	3	4						
zu:	*a*	*a*	*b*	*c*	*d*	*e*	*f*	*g*
Fe ...	63·69	26·6	25·24	21·45	21·87	22·30	31·02	28·07
Ni ...	33·97	75·2	74·17	76·60	76·16	76·48	67·63	71·93
C ...	—	—	—	—	—	—	—	—
Co ...	1·48	—	0·46	1·19	1·37	—	0·70	—
Mn ...	—	—	—	-	—	—	—	—
Cu ...	—	—	—	0·66	0·49	1·22	—	—
Pt ...	—	-	-	—	-	—	—	—

1*a*. М. Ларіоновъ (Larionow Halbinsel), Русскій Островъ (Russische Insel), Бладивостокъ (Vladivostok). Aus Quarzporphyr. C. A. Яковлевъ (S. A. Yakovlev) anal. bei A. A. Иностранцевъ (A. A. Inostrantzev), Trav. Soc. Imp. Natur. St. Pétersbourg, 1907, vol. 35, no. 5, sect. géol. min., pp. 21 (Russ.) and 49 (Deutsch).

1*b*. Ovifak. J. L. Smith, Ann. Chim. Phys., 1879, vol. 16, p. 452.

2*a*. St. Josephs Island, Lake Huron, Canada. G. C. Hoffmann, Geol. Surv. Canada, Ann. Rep., 1892; abstr. Zeits. Kryst. Min., 1894, vol. 23, p. 507.

2*b*. Березовск (Berezovsk), Ural. A. Daubrée and S. Meunier, Compt. Rend. Acad. Sci. Paris, 1891, tom 113, p. 172.

2*c*. Санарка (Sanarka), Ural. C. Schmidt anal. bei C. Grewingk, Arch. Naturk. Liv.-Est.-Kurlande, 1882, vol. 9, p. 150.

2*d*. Weaubleau, Hickory Co., Missouri. E. T. Allen, Amer. Journ. Sci., 1897, ser. 4, vol. 4, p. 99.

2*e*. Holden, Jackson Co., Missouri. *Idem, ibid.*

2*f*. Choceň (Chotzen), Československo. J. G. Neumann, Jahrbuch k. k. Geol. Reichsanst., 1857, vol. 8, p. 355.

3*a*. 'Catarinite', Santa Catharina, Brazil. A. A. Damour, Compt. Rend. Acad. Sci. Paris, 1877, vol. 84, p. 478.

4*a*. R. Elvo, Biella, Piedmont, Italia. Mattirolo anal. bei A. Sella. Compt. Rend. Acad. Sci. Paris, 1891, vol. 112, p. 171.

4*b*. Josephine Co., Oregon. G. S. Jamieson, Zeits. Kryst. Min., 1906, vol. 41, p. 157.

4*c*. South Fork, Del Norte Co., California. *Idem, ibid.*

4*d*. Hoole Canyon, Pelly River, Yukon. R. A. A. Johnston, Summ. Rep. Geol. Surv. Dept. Mines, Canada, 1911 for 1910, p. 258.

4*a*. Fraser River, British Columbia. F. G. Wait, anal. bei E. C. Hoffmann, Amer. Journ. Sci., 1905 ser. 4, vol. 19, p. 319.

4*f*. Gorge River, Awarua Bay, New Zealand. W. Skey, New Zealand Inst. Trans., 1885, vol. 18, p. 401.

4*g*. Бобровка (Bobrovka), Ural. Н. К. Высоцкій (N. K. Vysotzky), Mem. Com. Geol. St. Pétersburg, 1913, ser. 2, vol. 62, pp. 106 (Russ.) and 667 (Deutsch).

veining not only the broken-down remains of older silicates but also the products of serpentinization. In these it is occasionally recognizable as of younger formation. Especially striking are loose, mossy distributions often passing over into skeletons and pseudomorphous structures after a cubic mineral. The occurrence of zoned, botryoidal structures with magnetite and gangue and even with limonite furnishes important evidence, and the association of (Ni,Fe) with native copper (sometimes in repeated alternations) is decisive. [i.e. of the recent formation of the (Ni,Fe).]

The genetic interpretation is difficult. Purely supergene reduction, perhaps under bogs, must be excluded. A thermal origin in the temperature range of talc formation is the most probable. Anyhow sulphides occur in association, and they are derived from an older but certainly not an orthomagmatic period. These sulphides already show a replacement series with increasing Ni content. The presence of nine such sulphides has been established, and only a few of them can be identified satisfactorily with commoner minerals. Although some are similar to well-known ores, they show a partial substitution of iron by nickel. Finally two or three are clearly sulphides of copper and nickel, not hitherto known as minerals.

One can assume, then, that native nickel-iron (Ni,Fe) is relatively widely distributed in serpentine areas but that its grains escape notice because of their minute size. The (Ni,Fe) alloys are only readily recognized when they are associated with valuable placer minerals in sand or when they are of unusual size or frequency.

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Verzeichnis der Abbildungen (Plates IV–VIII)

Plate IV, Abb. 1. Josephinit formt eine körnige Struktur ab. An den Korngrenzen etwas Magnetit (dunkelgrau, hart). An den Korngrenzen ist der sonst sehr porige Josephinit stellenweise kompakt. Vergr. 40 ×.

Abb. 2. Eigentümliche Ballenstruktur des sehr porigen Josephinit. An den Korngrenzen (fast schwarz) Gangart. An einer Stelle (links ein) Relikt von Sulfid III (lichtgrau, porenfrei). Vergr. 80 ×.

Abb. 3. Einzelheit aus der Probe der Abb. 1. (Ni,Fe) in eisblumenartigen Skeletten. Schwarz sind teils Hohlräume, teils Gangarten. Vergr. 400 ×.

Abb. 4. Ähnlich Abb. 3, aber Formen mehr moosig, nicht fiederförmig. Vergr. 400 × (Ölimmersion).

Abb. 5. Feines Netzwerk von (Ni,Fe) in Olivinfels (dunkelgrau); in letzterem sind rundliche bis idiomorphe Magnetit Kristalle (lichtgrau) eingelagert. (Ni,Fe) auch in gröberen kompakten Massen, von denen anscheinend das Netzwerk ausgeht. Vergr. 100 ×.

Abb. 6. Teils kompaktes, teils lockeres, teils sehr feinporiges (Ni,Fe) mit geregelt eingelagertem Chlorit (oder Talk), letztere praktisch schwarz. Vergr. 100 ×.

Plate V, Abb. 7. Ähnlich Abb. 6. Der Anteil von Silikat ist erheblich geringer. Vergr. 40 ×.

Abb. 8. (Ni,Fe) pseudomorph nach dem Lamellenwerk eines grobkörnigen kubischen Minerals. Schwarz sind Löcher, sehr dunkelgrau sind Gangart-Einschlüsse. Vergr. 120 ×.

Abb. 9. Josephinit (reinweiß) umgibt rhythmisch mit Zwischenlage von Gangart (schwarz) u. Magnetit (grau), der massenhaft feine Verdrängungsrelikte von Sulfid (weiße Durchstäubung) enthält. Ganz außen, wieder Jos., getrennt durch eine Gangpartie, eine rhythmische Kruste von Brauneisen und Andeutung einer zweiten. Vergr. 200 ×, Ölimmersion.

Abb. 10. Kompaktes (Ni,Fe) wächst von Klüften aus idioblastisch in das (Ni,Fe)-Moos hinein. Vergr. 120 ×.

Plate VI, Abb. 11. Ähnlich wie Abb. 8, Lamellen aber breiter und alle Formen regelmäßiger. Am Rande links oben etwas Magnetit. Vergr. 50 ×.

Abb. 12. Ähnlich Abb. 8 u. 11. Die Lamellen sind hier streifigporig aufgebaut, die Zwickel zum Teil mit jüngerem (Ni,Fe), das eine im Photo nicht erkennbare Spur abweichend gefärbt ist, erfüllt. Vergr. 500 ×, Ölimmersion.

Abb. 13. Lamellenwerk ähnlich Abb. 10-12, das aber hier aus Magnetit besteht, während (Ni,Fe) in wechselndem Anteil neben Silikat die Zwickel füllt. Vergr. 120 ×.

Abb. 14. Rekristallisation am 'gehämmerten' Rand des Gerölls. Rekristallisiert sind (Ni,Fe) weiß, Kupfer schwer abtrennbar, reinweiß, Magnetit, dunkelgrau, Chalkosin, sehr dunkelgrau, 'Chalkopyrrhotin' mit eben erkennbarem Valleriitzerfall, lichtgrau, zum Teil mit spinnennetzähnlichem Muster. Vergr. 180 ×, Ölimmersion, starkes Rotfilter.

PLATE VII, Abb. 15. Gediegen Kupfer (reinweiß) fleckig verteilt in wechselnder Altersbeziehung im (Ni,Fe) (lichtgrau). (Ni,Fe) hat eine größere Neigung zu idiomorpher Entwicklung. Vergr. 500 ×, Ölimmersion, starkes Rotfilter.

Abb. 16. (Ni,Fe) kompakt mit unverdauten Verdrängungsrelikten von IV (dunkelgrau, durch Pleochroismus etwas verschieden). Löcher an der Stelle herausgebrochener oder verdrängter Sulfide. Vergr. 125 ×.

Abb. 17. Verdrängung von Sulfiden, überwiegend III (vergl. Korn mit Sprüngen in der Mitte!). (Ni,Fe) als Verdränger dieser Sulfide ist viel geschlossener als sonst. Vergr. 500 ×, Ölimmersion.

Abb. 18. Sprünge, teils offen, teils gangerfüllt formen eine alte Struktur ab. Verdrängungsreste von III nur selten erhalten, meist sind Löcher der Platz ehemaliger Relikte. Vergr. 200 ×, Ölimmersion.

PLATE VIII, Abb. 19. (Ni,Fe) mit Verdrängungsrest von III, das hier in den Eigenschaften etwas abweicht (Ähnlichkeit mit VI) und auch etwas Cu (reinweiß) liefert. Vergr. 400 ×, Ölimmersion, starkes Rotfilter.

Abb. 20. Sulfidrest (III) in porigem, zum Tiel fast moosartigem (Ni,Fe). Vergr. 200 ×, Ölimmersion.

Abb. 21. Größerer Sulfidrest im (Ni,Fe). Das dunklere Sulfid IV wird von dem isotropen hellerem III verdrängt. (N.B. die Aufnahme ist auf ganz starken Kontrast gearbeitet). Vergr. 180 ×, Ölimmersion.

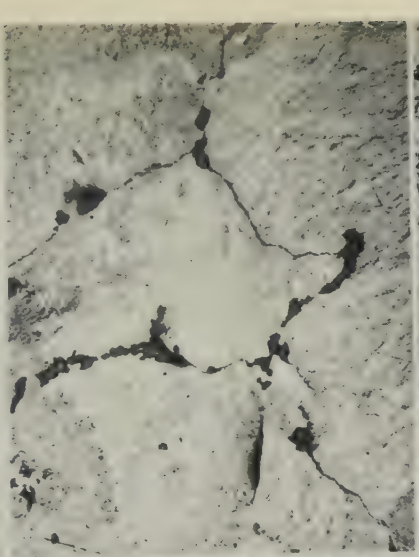
Abb. 22. Verschiedene Sulfide in (Ni,Fe) und Cu (Cu, besonders links, ist hier schwer von (Ni,Fe) zu unterscheiden). Sulfid VI (mittelgrau) ist von einem Netz von VIII durchsetzt und wohl von ihm verdrängt. Links ist eine mit 'Valleriit' durchzogene etwa sanduhrförmige Partie von III (lichtgrau), in der Mitte und mehrfach sonst, zum Teil VI bezw. VIII säumend, findet sich reichlich IX. Vergr. 180 ×, Ölimmersion, Rotfilter.

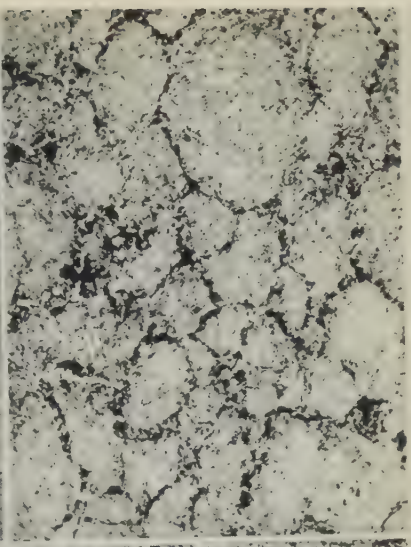
Abb. 23. Einzelheit aus Abb. 26. Verdrängungsrest von III, dessen Sprünge (hier durch Anlaufen noch betont) parallel mit dem Netzwerk in dem verdrängten Kristall laufen. Vergr. 400 ×, Ölimmersion.

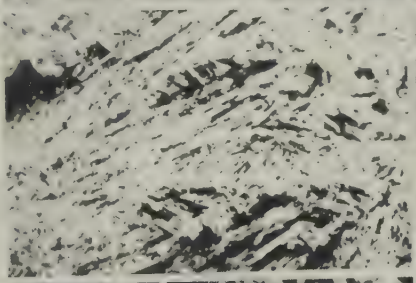
Abb. 24. Pseudomorphose nach einem großen Korn eines kubischen Minerals. Netzwerk von (Ni,Fe) und Magnetit; die Zwickel sind teils mit Gangart (sehr dunkel grau) erfüllt, teils leer. Außen folgt zunächst eine Zone von besonders kompaktem (Ni,Fe). Vergr. 120 ×.

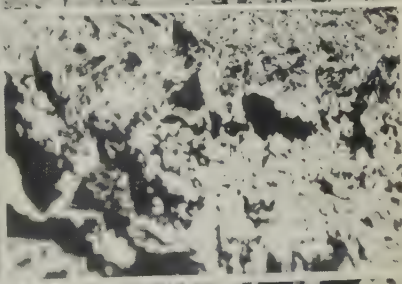
Abb. 25. (Ni,Fe) verdrängt Magnetit, der strichförmige Sulfidteilchen enthält als Relikte eines bereits von ihm verdrängten entmischten Sulfids. In Gangart lagern die Körner genau wie im Magnetit. Vergr. 200 ×, Ölimmersion.

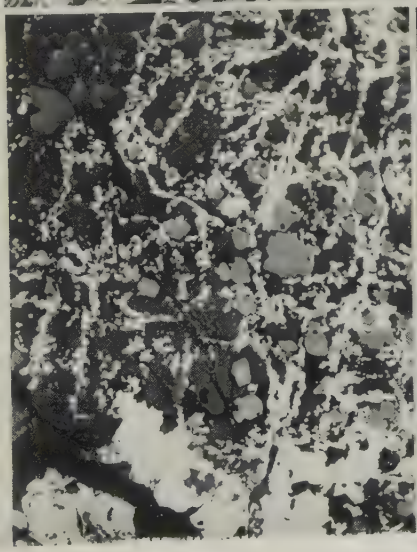
The cost of plates IV–VIII is met by the Miers Memorial Fund.











P. Ramdohr: Josephinite, awaruite, and souesite

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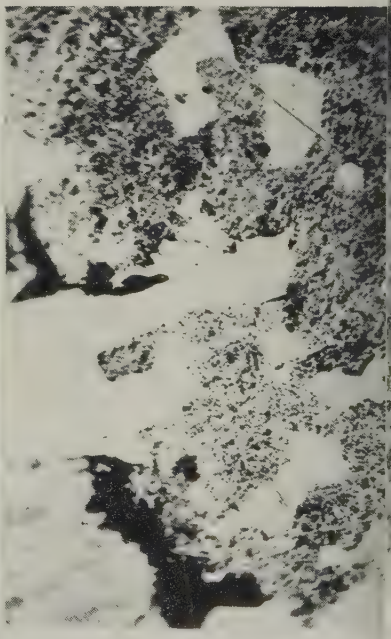

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P. Ramdohr: Josephinite, awaruite, and souesite

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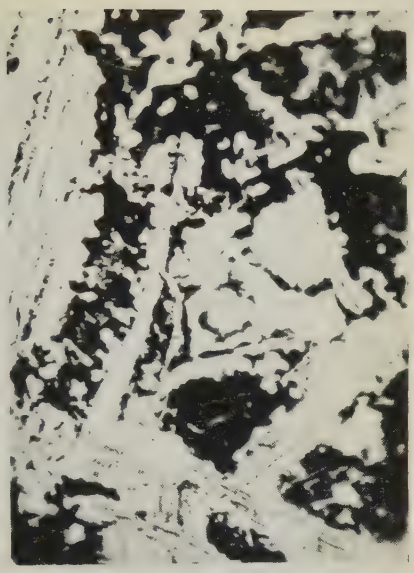

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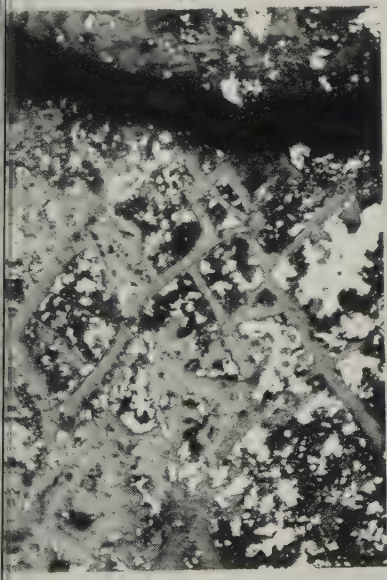

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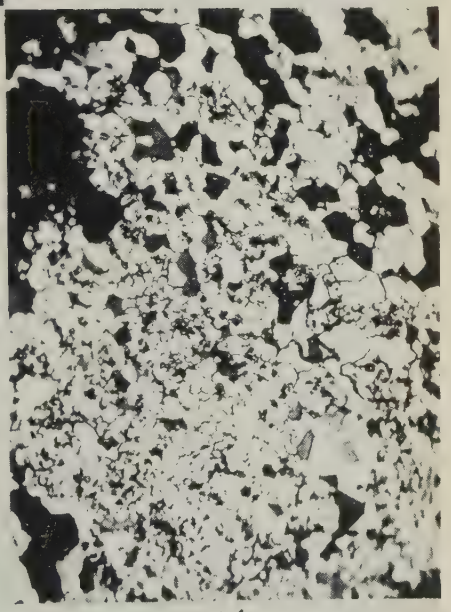

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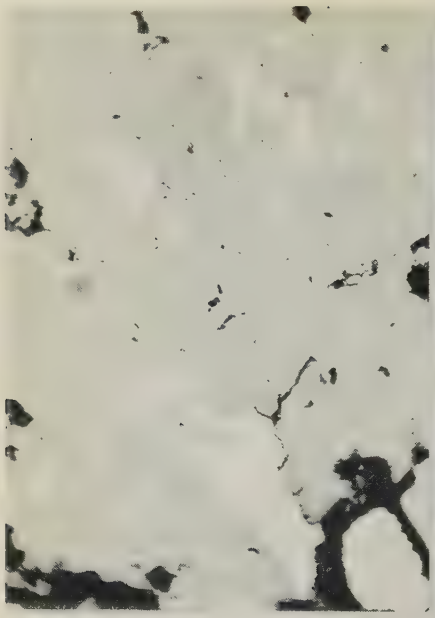
P. Ramdohr: Josephinite, awaruite, and souesite



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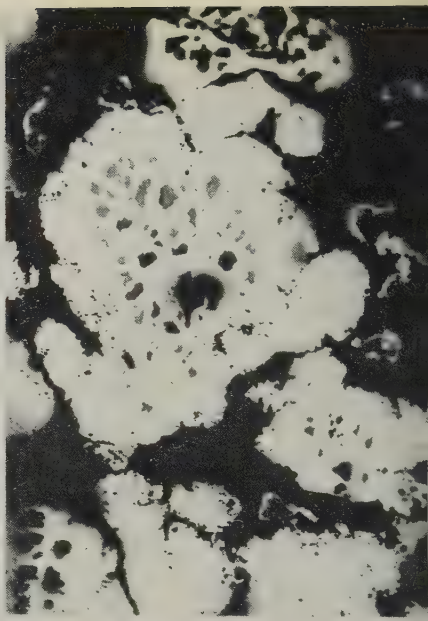

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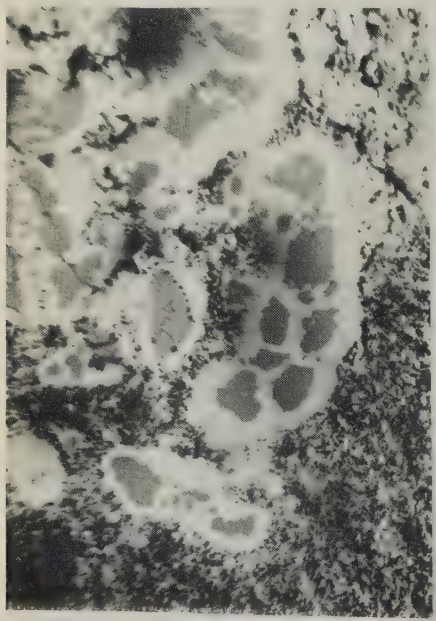

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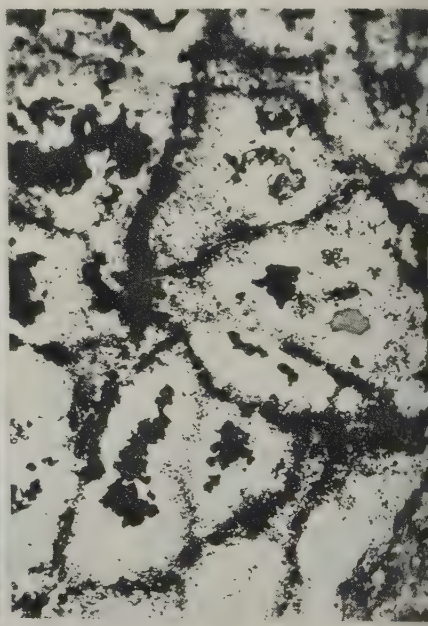

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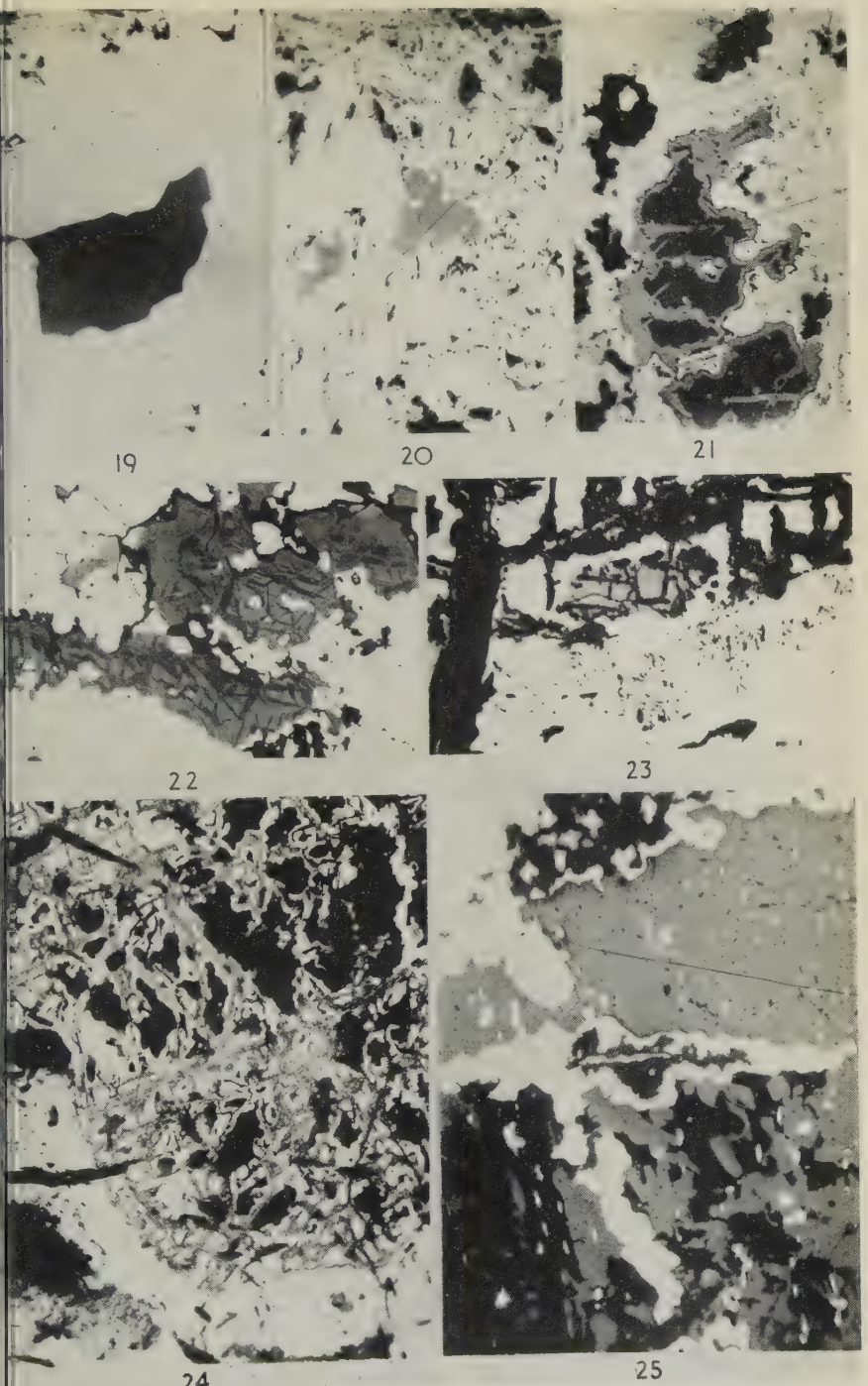
P. RAMDOHR: JOSEPHINITE, AWARUITE, AND SOUESITE



P. Ramdohr: Josephinite, awaruite, and souesite

John Henry Heuland

By Sir Arthur Russell, Bart.

JOHN HENRY HEULAND, Fellow of the Geological Society, mineral collector and dealer of 25 King Street, St. James's, London, was born in 1778. He moved in 1839 to 31 Red Lion Square, London, where he remained until after 1850. Few details of his life are known, but his sale catalogues and his intense activity as a collector and dealer during the period when it was fashionable to form collections of minerals have secured him an important place in the historical archives of mineralogy.

In what year Heuland began to deal in minerals is uncertain, but it was before 1804 when we have a record of his buying in Lisbon. He subsequently travelled through France, Germany, Sweden, and Russia, collecting and buying minerals wherever possible. About the year 1806 he came into the possession of a fine collection of minerals which had been formed on the Continent between the years 1766 and 1806 by his uncle Mr. Jacob Forster. To this collection Heuland made valuable additions until 1820, when he sold it to Mr. Charles Hampden Turner, of Rooksnest, Godalming, Surrey. Subsequently the collection became the property of Henry Ludlam, who on his death bequeathed it to the Museum of Practical Geology, London. In the same year Heuland entrusted Armand Lévy, then resident in London, with the making of an elaborate *catalogue raisonné* of this collection, based on the system of Haüy, and to be accompanied by an atlas of crystal drawings. Lévy commenced the work and continued it at Brussels, where he had gone to live. In 1828, however, he took up a professorship at Liége, and did nothing further to the catalogue, although, as Heuland indignantly states in the preface, he (Lévy) had received from him £2,000 in emoluments. In 1832 Lévy returned to France, and Heuland, on the advice of H. J. Brooke and his son Charles Brooke, entrusted the execution of the remaining 34 plates to a Mr. M. E. Brookes, the three volumes in French and atlas of plates being eventually published in London in 1837.[1]

In 1814 Heuland was buying from a Monsieur Lelièvre (Le Lièvre) in Paris, and during the next few years was holding sales in that capital.

In addition to the above-mentioned collection, Heuland formed

[1] A. Lévy, Description d'une collection de minéraux, formée par M. Henri Heuland, et appartenant à M. Ch. Hampden Turner, de Rooksnest, dans le Comté de Surrey en Angleterre. Londres, 1837, 3 vols. and atlas of plates, pp. i–iv.

another, even more important collection of his own numbering some 7,013 extremely choice specimens. In this was incorporated the fine collection of the Marquis de Drée, which he had purchased in Paris about 1826. The specimens belonging to this collection of Heuland's all

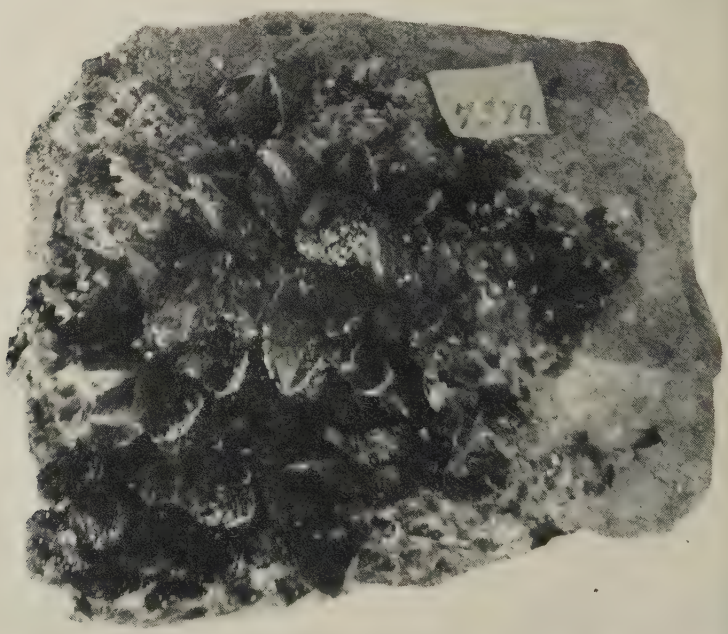


Fig. 1. Amethyst, crust of pyramidal crystals dusted with chalybite. Porkura, Transylvania, Romania, showing a Heuland label no. 7379; (B.M. 92126).

bore very characteristic boldly written numbers on rectangular labels (fig. 1) and very many of these are to be seen in the British Museum and other collections of importance. The manuscript catalogue of this collection, in Heuland's handwriting, came into the possession of Mr. John Calvert, and from him passed to Mr. Albert F. Calvert, but is now, unfortunately, lost, or at any rate, inaccessible.[1] Extracts from it relating to Heuland's specimens in the Mineral Department of the British Museum were made by Mr. Thomas Davies in 1873, and are preserved in two note-books. This collection was eventually disposed

[1] The writer has made repeated efforts to discover the whereabouts of this catalogue, including inquiries of Mr. Albert F. Calvert, but to no avail.

of piecemeal by Heuland along with specimens from other sources at his periodic sales. He had rapidly become the foremost dealer in Europe, adopting the excellent rule of handling only first-class specimens. Heuland was a good linguist and bought largely from individuals and at sales on the Continent, and was evidently an excellent judge of good minerals: he was, moreover, most careful to obtain, as far as possible, accurate localities with his specimens. His sale catalogues make most tempting reading. Evidently he had a rich and most enthusiastic clientèle, private mineral-collecting having reached its zenith in this country in the first half of the nineteenth century. His descriptions of the specimens are often quaintly elaborate, and sometimes, to say the least, somewhat exaggerated. The following are examples, and show the high prices certain specimens realized, although others, such as meteorites, fetched comparatively small sums.

'Red Tourmaline from Perm; in Siberia—to be put up at £50. This specimen has cost the late Mr. Forster £62. 10. 0, and Mr. H. can easily dispose of it for that sum in Russia. Since the burning of Moscow this is the largest specimen known, and the English Mineralogists having visited St. Petersburg or Moscow, will have convinced themselves of the value of this variety of the Tourmaline; it may be well to observe that but one specimen has ever been found, and that the few existing in the collections come from it, having been broken with the intention to divide it amongst the collectors, though, as already said, at enormous prices.' (Sale Catalogue, May 10, 1830, Lot 400.)

'The richest specimen raised of filiform Native Silver, from the mine Wheal St. Vincent, in the parish of Calstock, Cornwall, weight 50 ounces; cost the intrinsic value of £13. 15., at which price it is to be put up.' (Sale Catalogue, May 2, 1831, Lot 273.) This specimen remained unsold until the sale of May 13, 1839, Lot 997, when it found a purchaser.

'The finest specimen in this or any other country of Native Sulphur from Conilla, near Cadiz, Spain, in the highest preservation and of divers modifications of the primitive form; to be put up at £50. The King of Spain, Charles the IV gave a grant to the late uncle of Mr. H. (Mr. Jacob Forster) not only to work the mine, but also an edict that it should be closed after his selection was made; since that time, at the first siege of Cadiz, the place has been entirely destroyed. Far inferior Sulphurs to this lot from the said mine were sold in France and Russia from £100 to £200 a piece; and the late General Paris, of Paris, actually sent a special messenger to Cadiz to bring him a specimen which he bought unseen but by recommendation for one hundred louis d'ors.' (Sale Catalogue, May 2, 1831, Lot 712.) This specimen remained unsold until the sale of May 2, 1836, Lot 1,000, when it was put up with a reserve of £40, and sold privately to the British Museum (B.M. 57176) for that sum.

'Stalactitical Calcedony, from Bombay. A Christian Gentleman obtained this specimen for a certain number of rupees from an East Indian idolator while the latter was worshipping it. When Mr. H. obtained the specimen it was entirely besmeared with red ochre, which it appears is characteristic of these idols; to be put up at £10.' (Sale Catalogue, May 2, 1831, Lot 393.)

'The most magnificent specimen extant of the lenticular rose Carbonate of Manganese, on calcedony Quartz, Schneeberg, Saxony; to be put up at £12.' (Sale Catalogue, May 5, 1834, Lot 401.) This specimen actually realized £31.

'An invaluable specimen of prismatic and dentritic Phosphate of Lead, Hofsgrund, Breisgaw; to be put up at £30. The eye can alone do justice to the indescribable beauty of this treasure.' (Sale Catalogue, May 5, 1834, Lot 824.) This specimen actually realized £33.

'The most valuable crystal known of the Idocrase, from Ala, Piedmont; cost 600 francs; to be put up at £24.' (Sale Catalogue April 14, 1834, Lot 820.) Actually bought by the Duke of Devonshire for £30.

'The Diaspore, of which but one specimen is known, and from which every other like this has been chipped by the late Mr. Lelièvre, selling the last and largest for 2,000 francs, to the College of Mines, Paris, he never gave the locality.'[1] (Sale Catalogue, May 13, 1839, Lot 830.)

'The finest and largest specimen of Malachite in England, from Gumosheffsky, Siberia,[2] to be put up at £100. In the year 1800, this slab was valued at £500 at St. Petersburg, and in 1808, Mr. H. could easily have disposed of it in London for £300.' (Sale Catalogue, May 15, 1843, Lot 200.)

In a letter of Heuland's dated May 11, 1839, he says: 'Mr. Turner (Charles Hampden Turner) took the chalcedony from Trevascus mine, Gwinear, Cornwall, for £35.' Many important specimens of meteorites passed through Heuland's hands, and in 1831 he presented a fragment of that from Bitburg, Rhenish Prussia, to the British Museum. He bought many Greenland minerals, then great rarities, from Sir Charles L. Giesecke, and American minerals from Professor C. U. Shepard of Yale.

The following is a list of the Heuland sale catalogues known to the writer. It is obviously incomplete as to certain of the earliest, and also as to several of the later. All of these sales, with the exception of a few of the earliest, took place at 38 King Street, Covent Garden, London, under Messrs. Stevens and their predecessors. Some years ago the late Mr. F. N. Ashcroft fortunately obtained from Messrs. Stevens an incomplete series of these catalogues, which he most kindly placed at the writer's disposal, and which he subsequently presented to the Department of Mineralogy of the British Museum. All of Messrs. Stevens's other catalogues relating to the sales of minerals, of which they handled nearly all the important ones, have probably been destroyed along with the firm's early ledgers by a past employee.

List of Henry Heuland's Sale Catalogues.

1808. Mar. 16. 7 days' sale, 800 lots. 'A very select collection of minerals, chiefly from South America and Siberia.' Total realized £605. 3*s*. 6*d*. A copy of this catalogue is in the Mineral Department, British Museum, with the prices marked.

[1] Probably Urals, Russia.

[2] Gumeshevsk, U.S.S.R.

[1809] Specimens bought at a Heuland sale of this year with an invoice of their prices were in the collection of Lady Elizabeth Anne Coxe Hippisley of Stone Easton Park.

1812. May 4. 8 days' sale, 1,121 lots. Held at Mr. Christie's Great Room, Pall Mall, London. 'An extensive and most valuable collection of minerals, consisting of new substances almost without exception, and of those which are no longer to be found.' Among the buyers at this sale was Robert Ferguson of Raith, Kirkcaldy, Fifeshire. A copy of this catalogue is in the possession of the writer.

1815. Apr. 24. 6 days' sale, 820 lots. Held at Messrs. King & Lachée, 38 King Street, Covent Garden. A copy of this catalogue is in the possession of the writer.

1816. Mar. 25. Part I, 6 days' sale, 748 lots.
1816. Apr. 1. Part II, 5 days' sale, 600 lots.
1816. Apr. 22. Part III, 6 days' sale, 816 lots.

Copies of these three catalogues in the possession of the writer. Robert Ferguson from Raith a buyer from Part III.

1820. May 1. 6 days' sale, 775 lots. A copy of this catalogue in the British Museum (Bloomsbury) has the prices marked and the buyers names, who include Dr. Simmons, W. Lowry, Lady Aylesford, and J. Williams.

[1821]

1824. Apr. 30. 4 days' sale, 602 lots. A copy of this catalogue in the British Museum (Bloomsbury) has the date partly obliterated and is entered in the Museum catalogue as 1821. The prices only are marked.

1826. Apr. 10. 6 days' sale, 1 150 lots. 'A splendid and most Select collection of foreign Minerals, formed from a portion of The Marquis de Drée's and the duplicates of Mr. Heuland's private collection, including many large specimens for Public Museums and Shew Cabinets.' A copy of this catalogue is in the possession of the writer.

[1826. July 25.]

1829. May 4. 6 days' sale, 1,020 lots. Total realized, £1,955. 16*s*. This included specimens from Heuland's private collection. A copy in the Mineral Department, British Museum, has the prices and buyers marked.

1830. May 10. 3 days' sale, 600 lots. All from Heuland's private collection. Copies in the Geological Society's library, and in the Mineral Department, British Museum.

1830. May 31. 3 days' sale, 510 lots. All from Heuland's private collection. A copy in the Mineral Department, British Museum.

[1830. June 2.]

1831. May 2. 4 days' sale, 714 lots. All from Heuland's private collection. A copy in the Mineral Department, British Museum.

1832. May 14. 4 days' sale, 715 lots. All from Heuland's private collection. A copy in the Mineral Department, British Museum.

1833. Apr. 29. 6 days' sale, 1,200 lots. Part from Heuland's and part from Lady Aylesford's collection. A copy in the Mineral Department, British Museum.

1834. Apr. 14. 3 days' sale, 610 lots. Total realized, £304. 3*s*. 6*d*. Part from Heuland's and part from Lady Aylesford's collection. A copy in the Mineral Department, British Museum, has the buyers and prices marked and a note in Heuland's handwriting referring to the numbers on the specimens.

1834. May 5. 5 days' sale, 840 lots. Total realized, £1,669. 0*s*. 0*d*. A copy in the library of the Geological Society of London.

1835. May 11. 5 days' sale, 1,002 lots. A copy in the Mineral Department, British Museum.

1836. May 2. 5 days' sale, 1,025 lots. Part from Heuland's and part from Lady Aylesford's collection. A copy in the Mineral Department, British Museum, has some of the prices marked.

1837. June 12. 5 days' sale, 1,002 lots. Part from Heuland's and part from Lady Aylesford's collection. A copy in the Mineral Department, British Museum, has some of the prices marked.

1837. Dec. 11. 2 days' sale, 500 lots. Including 'a choice collection of iron ores, the property of a Gentleman in the East Indies'. A copy in the Mineral Department, British Museum, has some of the prices marked.

1838. May 14. 4 days' sale, 837 lots. Part from Heuland's and part from Lady Aylesford's collection. A copy in the Mineral Department, British Museum.

1839. Feb. 18. 2 days' sale, 407 lots. Total realized £186. 2*s*. 0*d*. A copy in the Mineral Department, British Museum, has the prices and buyers marked.

1839. May 13. 5 days' sale, 1,048 lots. Part from Heuland's and part from Lady Aylesford's collection. A copy in the Mineral Department, British Museum, has most of the prices marked.

1840. May 4. 3 days' sale, 630 lots. A copy in the Mineral Department, British Museum.

1841. Jan. 12. 2 days' sale. A copy in the Mineral Department, British Museum.

1841. May 10. 2 days' sale, 456 lots. A copy in the Mineral Department, British Museum.

1842. May 9. 4 days' sale, 821 lots. This included the collection of Mr. Hazelwood. A copy in the Mineral Department, British Museum, has a few of the prices marked.

1843. May 15. 3 days' sale, 600 lots. A copy in the Mineral Department, British Museum.

1844. May 13. 2 days' sale, 420 lots. A copy in the Mineral Department, British Museum.

1844. July 16. 1 day sale, 222 lots. A copy in the Mineral Department, British Museum.

1846. Feb. 16. 2 days' sale, 400 lots. A copy in the Mineral Department, British Museum, has most of the prices marked.

1846. May 18. 5 days' sale, 1,002 lots. Total realized £803. 2*s*. 6*d*. A copy in the Mineral Department, British Museum, has the prices and

buyers marked. Dr. G. Troost of Philadelphia (1776–1850) bought largely at this sale.

1847. Mar. 15. 2 days' sale, 400 lots. Total realized £221. 6*s.* 6*d.* A copy in the Mineral Department, British Museum, has the prices and buyers marked.

1847. June 14. 2 days' sale, 400 lots. A copy in the Mineral Department, British Museum.

1848. Apr. 14. 1 day sale, 200 lots. A copy in the Mineral Department, British Museum.

N.B. For the years enclosed in square brackets there is known to have been a sale, but the catalogues have not been seen by the writer.

In many cases specimens which were sold appear again in later sales, Heuland having bought up the collections of his former clients. Among these were those of Lady Aylesford, Mr. Hazelwood, and Sir Francis L. Chantrey, F.G.S., F.R.S., the sculptor. It has been recorded that Heuland, knowing that the Prince Consort had greatly admired Sir Francis's collection, obtained an interview with His Highness, and apparently might have effected a sale, had not Queen Victoria come in at the critical moment, and, on hearing the price asked, £1,000, told the Prince he could not afford it, Heuland being abruptly dismissed.[1]

A number of letters from Heuland to Charles König, Keeper of Minerals in the British Museum, are preserved in the Mineral Department (fig. 2). An interesting letter also of Heuland's to His Excellency Sir Edward Thornton (1766 1852), Minister to Portugal, dated London, May 15, 1821, came with the C. H. Turner collection to Henry Ludlam, and is preserved along with the latter's papers in the Museum of Practical Geology. In this letter Heuland begins by speaking of the value set on 'rejected' Brazilian diamonds which he had received from the Portuguese Government. He goes on to say 'What I require is a first quality diamond of 16 carats' and for which he was prepared to send minerals to the value of £600 in exchange.

"The Brazilian objects I long to possess are the green Tourmaline with *summits* only, the Chrysoberyl in perfect crystals, the Euclase and the beryls with *summits*. The yellow topaz I had from the Marquis of Angaga is matchless, and Mr. Chamberlain never saw the like at Rio de Janeiro. I have some hopes of getting the refusal of his two crystals of beryl with pyramids and his immense large fragment of Euclase, but he makes me long too much for them, and has nearly tired out my patience. I have no objection to give him a very excellent price, if he will name one at once in the reach of my limits and of justice. I lately sold for him his water-worn Chrysoberyl to Mr. Henry Philips Hope (the well-known collector of pictures and precious stones) for £250. It was less valuable in the rough, and I advised him to have it cut; he did so, and besides a small stone, it gave a perfect one of 44 carats. Speaking of Mr. Hope, I beg to inform Your Excellency that he is most anxious to

[1] E. G. Allingham, A Romance of the Rostrum. London, 1924, pp. 35–36.

Monday 6th May 1839.

My dear Sir,

After I had the honor of seeing you, I went to the Marquis of Northampton, who received me with great affability. He expects to meet you at the Royal Society on Thursday; Friday he intends going to the Sale room, and most assuredly will speak to you with regard to your kind recommendation of the opportunity to the

Charles König Esq^re &c &c &c.

FIG. 2. Letter from Henry Heuland to Charles König, F.R.S

Trustees. On Saturday morning the
Marquis leaves London. Let me
entreat you by the glory and interest
of the Collection under your guidance, not
to lose this time Lot 200, 400, 600
and 800, which lots, should you wish it,
can be withdrawn before the Sale, to save
a Bidding. I remain

My dear Sir

Yours most respectfully

Henry Hensleigh D.

Keeper of Minerals (including Fossils) 1837–51.

possess a diamond *perfectly* black, and he would go far to obtain that end. He has the finest collection of cut jewels in the world, and if Your Excellency should meet with any *quite extraordinary* Brazilian gem, I am confident I could place it for Her. [Apparently Lady Thornton was a collector of minerals, for Heuland speaks of sending her boxes of specimens, two lists of which are attached to the letter.] 'I am infinitely obliged to Your Excellency for the Meteoric iron from Bahia (Bendegó, Bahia, Brazil) which is now in Mr. Turner's collection, from which I took a smaller one which Your Excellency finds under Lot 575 in my mentioned sale (1821) with the price it fetched. It was bought by the British Museum, and the description I gave of it (according to Your Excellency's kind communication to me) was the reason it obtained such an extraordinarily high price, causing a great deal of good humour in the sale room at the time. Mr. Chamberlain possesses a specimen of 2 lbs. weight.'

Heuland wrote three short papers on minerals: 'On a Mass of Platinum at Madrid',[1] in which he gives an account of the history of a platinum nugget weighing 1 pound 9 ounces 1 drachm, found in 1814, near the mines (washings) of Don Ignaico Hurtado at Chocó, Colombia, South America, and which was presented to the King of Spain, who deposited it in the Royal Museum at Madrid. This paper also notes the discovery of two mines of precious opal in the district of Gracias a Dios, Honduras, and the receipt by Heuland of specimens from there, also the receipt of an undescribed meteorite from a spot 10 leagues inland from the coast at Omoa, Honduras. 'Account of some new Minerals' refers to helvite, Brothers Lorenz mine, Schwarzenberg, Saxony; albin (apophyllite); peliom (iolite); scorodite; tungstate of lead (stolzite) Zinnwald, Bohemia (the first reference to this species given in Dana, 6th edition, is Breithaupt, 1820); zircon on zoisite, Prickler Halt, Sau Alp, Carinthia.[2] 'Notice concerning the Matrix of the Brazilian Diamond' was read May 16, 1823.[3]

Heuland was elected a member of the Geological Society of London in 1813, becoming its foreign secretary in 1818, an office which he filled until 1828.[4] The mineral 'Heulandite' was named after him by H. J. Brooke in 1822 (Edinburgh Phil. Journ., vol. 6, p. 112).

In the latter part of his life Heuland resided at Hemel Hempstead, Hertfordshire, and died at 4 Pelham Place, Hastings, Sussex, on November 16, 1856, from 'softening of the brain' from which he had suffered for two years.

[1] Henry Heuland, Ann. Phil. (Thomas Thomson), 1818, vol. 12, p. 200.
[2] Henry Heuland, Ann. Phil. (Thomas Thomson), 1818, vol. 12, pp. 453, 454.
[3] Henry Heuland, Trans. Geol. Soc. London, 1824, vol. 1, p. 419.
[4] H. B. Woodward, The History of the Geological Society of London. 1907, pp. 72, 73; pp. 275 and 298.

By the terms of his will he bequeathed any minerals that remained in his possession to his wife, Frances Ann.

Heuland had two brothers, of whom Conrad, the younger, went out to Cochabamba, Peru, in 1793, as mineralogist to the Spanish Government, being accompanied by his elder brother who acted as his secretary. The elder died there of fever in 1806, and the younger had, in 1821, not been heard of for six years.

An interpretation of the composition of high-silica sericites

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Abstract: The high-silica sericites generally contain a corresponding appreciable quantity of a divalent element, usually magnesium, and their chemical composition is interpreted as being intermediate between that of muscovite, $KAl_2(AlSi_3)O_{10}(OH)_2$, and that of the equivalent high-silica mica leucophyllite, $KAlMg(Si_4)O_{10}(OH)_2$. The series muscovite-leucophyllite includes the named micas phengite (high-silica sericite), mariposite, and alurgite. Selected analyses are plotted and fall on a corresponding straight compositional variation line from muscovite to leucophyllite. It is shown diagrammatically that the analysed sample of mariposite probably contained about 8 % of quartz. It is recommended that the only species names in this series to be retained are those of the end members muscovite and leucophyllite. Their indices of refraction and specific gravities are very similar.

Introduction.

ANALYSES of many sericites agree closely with analyses of many muscovites, the difference in the two minerals being essentially in the state of physical aggregation. Other sericites contain a larger amount of silica than is contained in muscovite and have in part been termed phengite. These high-silica sericites generally contain more divalent elements (chiefly magnesium and iron) than those sericites whose silica content is about the same as that of nonsericitic muscovite. The reported high-silica content of those sericites with only very small amounts of divalent elements is probably due to admixed quartz. It is the purpose of this paper to emphasize this content of divalent elements in high-silica sericites as the basis for an interpretation of their chemical composition.

Mica formulae.

An interpretation of the composition of any mica must be based on the now well-known structural formulae of the micas, which can be generalized as $X.Y_{2-3}.Z_4.O_{10}(OH)_2$. X represents the large cations (Na, Ca, K, Ba, &c.), with an ionic radius of about 1·0 to 1·4; Y represents cations (Al, Fe, Mg, Li, &c.) in octahedral co-ordination, with an intermediate ionic radius of about 0·6 to 0·9; and Z represents cations (Si, Al) in tetrahedral co-ordination, with a smaller ionic radius of about

[1] Published by permission of the Director, U.S. Geological Survey.

0·4 to 0·6. Anions (O, F, &c.), with a large ionic radius of about 1·3 and larger, may substitute for hydroxyl. In the Y position a dioctahedral[1] formula has two cations with one vacant octahedral position,[2] and a trioctahedral formula has three cations with no vacant position. In the Z position are four cations with tetrahedral co-ordination. These are Si and Al and they may be either a tetrasilicic group (Si_4), a trisilicic group ($AlSi_3$), a disilicic group (Al_2Si_2), or a monosilicic group (Al_3Si).[2] Some examples of the end-member mica formulae, on this basis, are shown in the tabulation below.

Series (from one end-member formula to another end-member formula) exist in the micas either wholly within one of these groups or between two of them. Hence in a mica formula calculated from an analysis, the number of cations of an element need not be a whole number as the cations are in the end-member formulae listed below.

Some examples of end-member mica formulae.

Tetrasilicic:	
Polylithionite	$K.LiLiAl.Si_4.O_{10}F_2$
Taeniolite	$K.LiMgMg.Si_4.O_{10}F_2$
Celadonite*	$K.Fe'''Mg^{o}.Si_4.O_{10}(OH)_2$
Leucophyllite†	$K.AlMg^{o}.Si_4.O_{10}(OH)_2$
Trisilicic:	
Muscovite	$K.AlAl^{o}.AlSi_3.O_{10}(OH)_2$
Phlogopite	$K.MgMgMg.AlSi_3.O_{10}(OH)_2$
Siderophyllite	$K.Fe''Fe''Fe''.AlSi_3.O_{10}(OH)_2$
Barium muscovite‡	$Ba.AlMg^{o}.AlSi_3.O_{10}(OH)_2$

* For this formula of celadonite see Hendricks and Ross (1941).

† This formula was referred to as alurgite by Stevens (1946), p. 106, on my suggestion, but as the analyses of leucophyllite are closer to the magnesium end-member of the muscovite-leucophyllite series (see fig. 1), this name seems preferable and is so used. Starkl (1883), p. 657, coined the name leucophyllite as a rock name for a phyllite with a glistening white colour and extraordinary fine platy structure However, apparently he considered the predominant component of the phyllite as one mineral, for he says: 'Die Härte des Minerals ist 1–2.' The sample analysed was '. . . möglichst reine quarzfreie Substanz . . .' Dana (1892), p. 616, uses the term leucophyllite as a mineral name for a variety of muscovite. Should future investigations show that Starkl's analysis was made on non-homogeneous material (mixture of sericite, talc, &c.) and the term leucophyllite become untenable as a mineral species name, then alurgite would be the name most applicable to what is here called leucophyllite.

‡ Not known as a mineral. A calcium muscovite would have a similar formula. The formula given for barium muscovite requires 31·06 % BaO and 8·17 % MgO. An analysis of a barium-containing muscovite from Franklin, New Jersey, described

[1] Following the nomenclature proposed by Stevens (1946).

[2] The writer has found it most useful, in studying various group formulae, to have in the formulae a symbol indicating a vacant position, and suggests a small open circle, raised halfway up in the line of type, such as °. This symbol is here used.

Disilicic:

Margarite	$Ca.AlAl^{o}.Al_2Si_2.O_{10}(OH)_2$
Magnesium margarite§	$Ca.MgMgMg.Al_2Si_2.O_{10}(OH)_2$
Ephesite‖	$Na.AlAlLi.Al_2Si_2.O_{10}(OH)_2$
Willcoxite¶	$Na.AlMgMg.Al_2Si_2.O_{10}(OH)_2$

Monosilicic:

Xanthophyllite	$Ca.AlMgMg.Al_3Si.O_{10}(OH)_2$

by Bauer and Berman (1933), shows 9·89 % BaO (and 6·33 % K_2O, 1·51 % Na_2O, and 0·36 % CaO) with 1·55 % MgO (and 1·84 % ZnO and 0·62 % MnO), and hence the mica analysed is of intermediate composition. Oellacherite is similar in composition.

§ Not known as a mineral. Brandisite and seybertite are intermediate members of the magnesium margarite-xanthophyllite (monosilicic) series.

‖ A new analysis of ephesite from Postmasburg, South Africa, made in the U.S. Geological Survey, has shown that the previous determinations of Li_2O are much too low. The mineral contains nearly 4 % of Li_2O and forms a series with margarite. A paper on the margarite-ephesite series, by W. T. Schaller and M. K. Carron of the U.S. Geological Survey is in preparation.

¶ A neglected member of the disilicic micas. Genth's analysis (Genth, 1873) shows a little iron and potassium. The atomic ratios for the analysis are: Z = 4·00 (1·98 Si and 2·02 Al); Y = 2·95 (0·99 Al, 0·07 Fe''', 0·14 Fe'', and 1·75 Mg; X = 1·06 (0·85 Na and 0·21 K); (OH) = 1·66.

The total charges of the cations in these formulae are 22. They may be distributed as follows:

	Large cation.	Octahedral group.	Tetrahedral group.
Tetrasilicic	1	5	16
	2	4	16
Trisilicic	1	6	15
	2	5	15
Disilicic	1	7	14
	2	6	14
Monosilicic	1	8	13
	2	7	13

Hence in going from trisilicic muscovite with 15 charges in the tetrahedral group to a tetrasilicic formula, such as that of leucophyllite, with 16 charges in the tetrahedral group, as long as the large cation (like potassium) remains monovalent, the charges in the octahedral group must be reduced from 6 to 5. This is readily accomplished by substituting one bivalent magnesium (or one ferrous iron) for one trivalent aluminium. As a high-silica mica must be in part tetrasilicic, there must also be present the corresponding amount of a bivalent element, to achieve compensation in the total cation charges. That is why high-silica sericites must contain the equivalent amount of magnesium or some other bivalent element of the proper ionic radius.

The composition of the high-silica sericites can be explained as being

members of a series from trisilicic muscovite, $KAlAl(AlSi_3)O_{10}(OH)_2$, to tetrasilicic leucophyllite, $KAlMg(Si_4)O_{10}(OH)_2$. The Si_4 in the leucophyllite formula accounts for the high silica and the Mg (or Fe″) accounts for the necessary presence of divalent elements.

We shall now see how the available data on the high-silica sericites agree with this explanation of their composition.

Discussion of chemical analyses.

Seven analyses are discussed. Except for the two analyses with highest percentages of SiO_2 and of MgO (namely, those of alurgite and leucophyllite), only analyses made in the U.S. Geological Survey are considered. Analyses of five varieties of pure sericite from Amelia, Virginia, are given by Glass (1935). As the analyses of two pairs of varieties are very close, their results are averaged:

1. Average of the analyses of the purple sericites, varieties 3 and 4 (Glass). Amelia, Virginia. R. E. Stevens, analyst.

2. Average of the analyses of the water-green sericite, variety 1, and of the maize-yellow sericite, variety 2. Amelia, Virginia. J. G. Fairchild, analyst.

3. White, claylike sericite from Melones, Calaveras County, California. U.S. Geol. Survey Chem. Lab. Record no. D–124 (no. 2). $2V = 0°$ to $10°r$. J. J. Fahey, analyst.

4. Marguerite-yellow to chalcedony-yellow sericite, variety 5. Amelia, Virginia. R. E. Stevens, analyst.

Additional analyses of high-silica sericites with several per cent. of MgO, which are very close to the analyses of the sericites from Amelia, are listed by Dana (1892) on pp. 618–619.

5. Green mariposite from Mariposa County, California, analysed by Hillebrand (1900). A second analysis of white mariposite from the same locality in which the ferrous and ferric oxides were not separately determined is very similar and hence is not used in this paper. As here shown, the green sample analysed contained about 8 % of quartz. According to Knopf (1929), p. 44, 'The mariposite-ankerite masses are generally traversed by a network of veinlets, consisting of coarse milky-white quartz.' He notes, on p. 38, the presence of rutile, accounting for the TiO_2, and states that mariposite is 'practically uniaxial', with a maximum value of 36° for 2E.

5*a*. The same analysis, after deducting 8 % of quartz and recalculating to 100 %. The method of arriving at the amount of quartz present is explained farther on.

6. Alurgite from San Marcel, Italy, analysed by Penfield (1893). This is the only one of the seven selected samples which does not have the fine scaly or fibrous texture with a silky or waxy luster commonly ascribed to sericite. Through the courtesy of Prof. Horace Winchell of Yale, some fragments of Penfield's type specimen (Brush collection no. 5523) were obtained. These fragments have β or γ indices of refraction about 1·597 to 1·600. Some scales were uniaxial, others had a 2V of 26°. Meixner (1939) obtained similar results.

7. Leucophyllite from Anna-Capelle, Austria, described and analysed by Starkl (1883). Analysis no. 49 on p. 619 of Dana (1892).

These seven analyses are reproduced in the tabulation below, to which are added the calculated percentage compositions of muscovite (first column) and of leucophyllite (last column) according to the end-member formulae given above. As will

be noted, there is a regular increase in the percentages of SiO_2 and of MgO (including FeO and MnO) with a corresponding decrease in the percentages of Al_2O_3 (including Fe_2O_3, Cr_2O_3, and Mn_2O_3).

Tabulation of selected analyses of high-silica sericites.

	M	1	2	3	4	5	5a	6	7	L
	Muscovite end-member	Sericites				Mariposite		Alurgite Italy	Leucophyllite Austria	Leucophyllite end-member
		Va.	Va.	Calif.	Va.	Calif.	8% quartz deducted			
SiO_2	45·26	46·81	47·64	49·37	49·16	55·35	51·39	53·22	57·11	60·57
Al_2O_3	38·40	35·97	32·07	29·21	30·81	25·62	27·81	21·19	19·80	12·85
Fe_2O_3	—	—	—	1·54	—	0·63	0·68	1·22	2·99	—
Mn_2O_3	—	—	—	—	—	—	—	0·87	—	—
Cr_2O_3	—	—	—	—	—	0·18	0·20	—	—	—
FeO	—	0·25	1·16	—	1·43	0·92	1·00	—	—	—
MnO	—	—	0·17	—	—	—	—	0·18	—	—
MgO	—	0·59	1·32	2·77	2·22	3·25	3·53	6·02	8·85	10·17
K_2O	11·82	10·16	9·05	9·72	10·90	9·29	10·08	11·20	3·39	11·87
Na_2O	—	0·64	0·09	0·14	0·48	0·12	0·13	0·34	1·42	—
H_2O^-	—	0·53	2·60	0·75	0·15	—	—	—	—	—
H_2O^+	4·52	5·03	5·56	6·88	4·73	4·52	4·91	5·75	6·30	4·54
etc.	—	0·30	0·12	0·19	0·19	0·25	0·27	—	0·49	—
	100·00	100·28	99·78	100·57	100·07	100·13	100·00	99·99	100·35	100·00

Plotting analyses quoted.

The percentage values for SiO_2, Al_2O_3, and MgO are plotted for each analysis on the rectangular diagram shown in fig. 1 as the three pairs of SiO_2 against Al_2O_3, SiO_2 against MgO, and Al_2O_3 against MgO. The three resulting points for each analysis should coincide and should lie on the straight line joining the similar points for end-member muscovite, $KAlAl(AlSi_3)O_{10}(OH)_2$(M), and for end-member leucophyllite, $KAlMg(Si_4)O_{10}(OH)_2$(L). As the values used for M and L are based on SiO_2, Al_2O_3, and MgO, it becomes necessary to recalculate the analyses considered on the same basis. Therefore the percentages of Fe_2O_3, Cr_2O_3, and Mn_2O_3 are calculated to their equivalent Al_2O_3; FeO and MnO to MgO; and Na_2O and CaO to K_2O. The resultant values are then recalculated to a basis of 100 %. The percentages so obtained, which are plotted in fig. 1, are as follows:

Recalculated percentages of SiO_2, Al_2O_3, and MgO.

Analyses	1	2	3	4	5	5a	6	7
SiO_2	46·48	48·01	49·33	49·26	55·60	51·74	53·57	56·92
Al_2O_3	35·72	32·30	30·17	30·87	26·26	28·54	22·69	21·63
MgO	0·73	2·08	2·77	3·03	3·79	4·12	6·16	8·82

In plotting the values for Al_2O_3 and MgO, the ordinates for MgO are used, whereas in plotting the values for SiO_2 and MgO, the abscissae for MgO are used.

The placements of the three points for each analysis gives some idea

as to the purity of the sample as they should coincide and fall on the line M–L, as they practically do for all analyses except those of mariposite (no. 5) and of leucophyllite (no. 7). The large circle necessary to

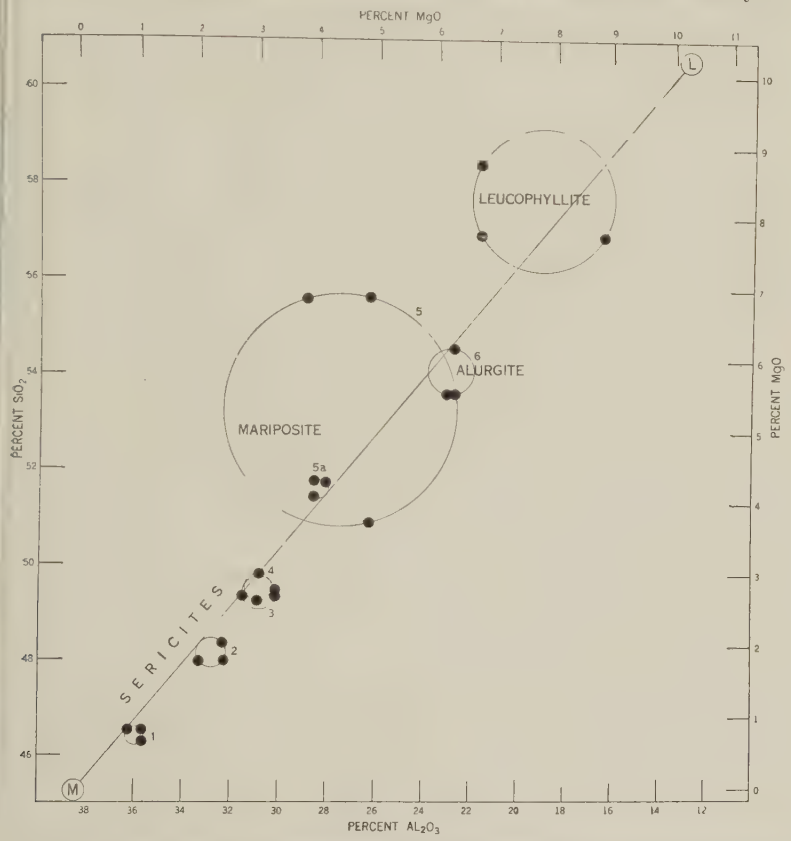

FIG. 1. Percentages of SiO_2 against Al_2O_3, SiO_2 against MgO, and Al_2O_3 against MgO, plotted as solid dots. The three dots for each analysis are then joined by a circle. For no. 4 two of the dots coincide. All three dots for each analysis should coincide and lie on the straight line joining the positions for end-member muscovite (M) and for end-member leucophyllite (L) if the sample analysed was homogeneous. The size of the circumscribed circle gives an estimate of the size of the impurities.

circumscribe the three dots for the analysis of mariposite (no. 5) indicates that the sample analysed was impure. As shown in fig. 2 the sample contained about 8 % of quartz. When this is deducted and the analysis recalculated to 100 % the resulting three dots (no. 5*a*) fall nearly on the line M–L and the resulting circle is very small.

The method of arriving at the conclusion that about 8 % of quartz was present in the sample of mariposite analysed by Hillebrand is as follows. His analysis was recalculated on the basis of deducting respectively 2, 4, 6, 8, 9, 10, 12, and 14 % of quartz, the three pairs of percentages plotted, and circles drawn through the three dots. The resultant circles indicate the extent of the impurities. If the circles are large, it is evident that the analysis is incorrect or that the sample analysed was impure.

By plotting the three points for the analysis of mariposite, after deducting the amounts of quartz stated, the circles first decrease in size, as shown in fig. 2, the smallest circle representing the results of deducting 8 % of quartz. If 9 % of quartz is deducted, the circles become larger again, indicating that 8 % represents closely the amount of quartz which must have been present in the sample analysed.

The three plotted points for alurgite (no. 6) fall closely on the M–L line and the resulting circle is small. Alurgite is closer to the leucophyllite end of the series than mariposite. Stevens (1946), p. 112, calculated the atomic ratios of Penfield's analysis to be: Z = 4·00 (3·59 Si and 0·41 Al); Y = 2·00 (1·27 Al, 0·06 Fe‴, 0·05 Mn‴, 0·01 Mn″, and 0·61 Mg); X = 1·00 (0·96 K and 0·04 Na); (OH) = 2·59. Alurgite is 59 % tetrasilicic leucophyllite and 41 % trisilicic muscovite.

For leucophyllite two analyses are given by Starkl (1883) with almost identical percentages of MgO but with about 4 % difference in the SiO_2 and nearly as much for Al_2O_3. These are analyses 49 and 50 as listed by Dana (1892) on p. 619. The presence of hydrated iron oxide, staining some flakes yellowish-brown, was noted by Starkl. Both analyses report nearly 3 % Fe_2O_3 with no determination of FeO. Plotting the values for the analysis with the lowest SiO_2 (52·81 %) resulted in such a large circle that evidently either the analysis is faulty or the sample was impure. Consequently this analysis is not further considered, though both the high SiO_2 and the high MgO show that its placement on the M–L line is near the leucophyllite end.

The second analysis by Starkl (no. 7 in fig. 1) with 57·11 % SiO_2 was made on material freed from quartz as far as possible. Applying the procedure used for interpreting the analysis of mariposite as made on a mixture of sericite and quartz did not yield similar results. The resultant circles, after deducting respectively 2 and 4 % of quartz, became larger instead of smaller, indicating that no quartz was present in the sample analysed. It is believed that the percentage of MgO reported is probably too high. The very low content of alkali with corresponding high

water, if correct, may be the reason that the three dots cannot be brought closer together. The low alkali content indicates a considerable trend

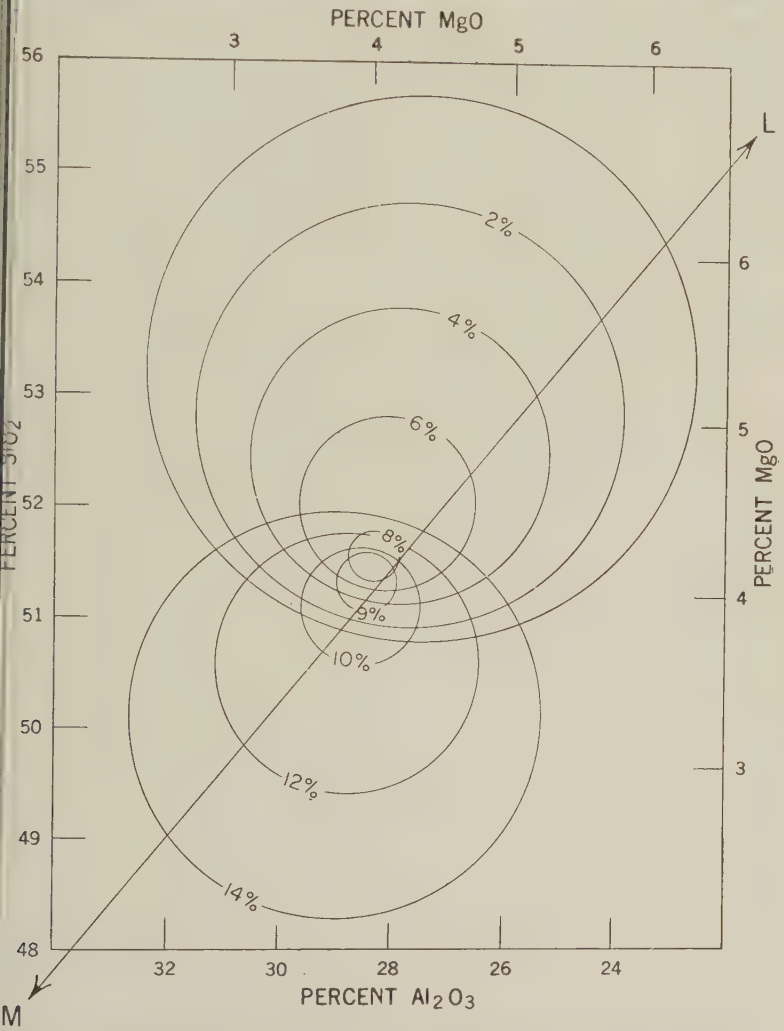

FIG. 2. The percentages of SiO_2, Al_2O_3, and MgO plotted as described for fig. 1 for the analysis of mariposite, after deducting respectively 2, 4, 6, 8, 9, 10, 12, and 14 % of quartz. The smallest circle joining each group of three dots is the one for 2 % of quartz; the largest circle represents the original analysis.

towards a hydromica. That the high-silica sericites show a definite trend towards the hydromicas is not confirmed by the other analyses plotted.

Both mariposite and alurgite are close to the middle of the M–L line and the two minerals are similar in composition, as previously noted by Schaller (1916), who suggested their essential identity. The so-called alurgite from Cajón Pass, California, described by Webb (1939), is not alurgite and is not simply a member of the muscovite-leucophyllite series. It is not a high-silica mica. It contains only 46·30 % SiO_2, whereas if it were a member of the muscovite-leucophyllite series, the 4·92 % of MgO + MnO present would require about 53 % of SiO_2. Meixner (1939), like Webb (1939), regards the red colour of the Italian alurgite as an essential property of alurgite. The writer prefers to regard the colour as an unessential property, depending on the presence of a relatively very small amount of a chromatic element. He would define alurgite as a part of the muscovite-leucophyllite series with necessary high-silica and the presence of an equivalent amount of divalent elements, usually magnesium. However, neither of the two names alurgite and mariposite deserves species rank. Both should be discarded, though for local interest the name mariposite will probably persist, as this green mica is so characteristically of widespread occurrence in the ankeritized rock derived from serpentine in the Mother Lode region of California. Alurgite is nearer the leucophyllite end of the muscovite-leucophyllite series and should be referred to as a variety of leucophyllite, should this name be adopted for the high-silica end-member of the series, with the formula $KAlMgSi_4O_{10}(OH)_2$.

It has not been possible to correlate systematically the variations in indices of refraction and in specific gravity with the variations in chemical composition for the members of the series. The indices of refraction of alurgite (the closest member of the series to leucophyllite for which data are available) are essentially those of muscovite. It has been stated that high-silica sericites have a very small axial angle, but so do some muscovites (see Axelrod and Grimaldi, 1949). Both the indices of refraction and specific gravity of muscovite and of leucophyllite are probably very close. The presence of small amounts of chromatic elements, such as Cr in mariposite and Mn in alurgite, probably causes a greater difference in the indices of refraction than that existing between muscovite and leucophyllite. Knopf (1929) gives the values of 1·60, 1·61, and 1·63 for the gamma index for different samples of mariposite.

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The statement of chemical analyses of stony meteorites and the interpretation of the analyses in terms of minerals

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In earlier analytical work on stony meteorites the analytical results were given in a number of different ways. Not only the principles, but also the methods used in the calculation of the mineral composition as derived from the chemical analyses, were of a different kind in almost every description of a stony meteorite. The same remarks of course apply to a certain extent also to the older descriptions of terrestrial rocks. The publications on the 'Quantitative [(American) system of] classification of igneous rocks' (1) and some publications by Henry S. Washington, especially a paper on 'The statement of analytical results of rock analyses' (2), contributed greatly to the unifying of the methods of representing the results of chemical analyses of rocks and calculating their mineral composition. Later on other systems for the statement and calculation of rock analyses have been introduced by other petrologists, especially by Paul Niggli, and all this work, taken together, has greatly contributed to clarification of the different ways in which the results of rock analyses can be stated and made use of in the petrological study of rocks.

With regard to the analyses of stony meteorites, there still remains to be done much the same work in respect of the establishment of the best ways of stating the results of chemical analyses and the ways of calculating the analyses in order to facilitate petrological comparison of the stony meteorites.

The fact that the abstracting of publications on meteorites has already been carried out for many years according to a well-devised plan has therefore been of very great help in the study of meteorites. It is to Dr. L. J. Spencer's comprehensive and clear abstracts of the meteorite literature during the course of several decades that we owe a good review of almost the whole of this literature during modern times, and this in spite of the very different ways in which a great deal of the original work has been published. Everyone who has studied meteorites during

This period has therefore been greatly indebted to Dr. Spencer for the great amount of work he has devoted to the abstracting of the literature on meteorites.

There has always been a wish to compare the chemical composition of stony meteorites with the composition of ultra-femic igneous rocks. It is therefore desirable that the analytical results for stony meteorites should—as far as possible—be presented in the same manner as the analyses of terrestrial igneous rocks. The principal differences between stony meteorites and igneous rocks arise from the content in stony meteorites of metallic nickel-iron and certain minerals which are chemically stable only in the presence of oxygen amounts insufficient to convert the oxidizable constituents into oxides. We can therefore say that the principal difference between the terrestrial igneous rocks and the stony meteorites is that the meteorites are oxidized in a lesser degree than are the terrestrial rocks.

The occurrence of more or less metallic nickel-iron and of certain minerals, which have so far not been met with in terrestrial igneous rocks, such as lawrencite, $FeCl_2$, oldhamite, CaS, daubréelite, $FeCr_2S_4$, and schreibersite $(Fe,Ni,Co)_3P$, however, requires a statement of the analytical results somewhat different from that of the terrestrial igneous rocks. Also chromite, $FeCr_2O_4$, and troilite, FeS, play a much more important part in stony meteorites than in igneous rocks, and phosphorus occurs in stony meteorites, according to our present knowledge, principally as a constituent of the lime-sodium phosphate merrillite, $3CaO.Na_2O.P_2O_5$, characterized some time ago by Shannon and Larsen (3).

When Berzelius in the early eighteen-thirties published his first analyses of meteorites he introduced the method of a separate determination of the chemical constituents soluble when the finely ground powder of the meteorite is treated with hydrochloric acid. This method was for a long time in quite general use, and is still employed by a great many analysts. It had already been early recognized that most of the stony meteorites are chiefly composed of olivine and rhombic pyroxenes, the olivine being soluble in hydrochloric acid, while this is not the case with the pyroxenes. The treatment with hydrochloric acid was therefore a means of separating the olivine from the pyroxenes, and thus afforded a way of determining the proportions of olivine and of pyroxenes in the rock. As we now know from a great number of analyses, the method is far from a quantitative one. This is due to several circumstances: firstly, an olivine, rich in iron silicate, is attacked by hydro-

chloric acid more easily and at a faster rate than an olivine rich in forsterite; secondly, the pyroxenes are not entirely insoluble in hydrochloric acid, the iron silicate also in this case being more readily attacked by the acid. In stones rich in iron silicates the proportion of orthosilicates, as determined by treatment with hydrochloric acid, will therefore appear comparatively larger than in stones poor in iron silicates. And further, the orthosilicates (olivines) are not the only constituents soluble in hydrochloric acid. In fact, in the chondrites rich in chondrules there are almost always considerable amounts of chondrules in which the olivines and the bronzites are embedded in a mesostasis of glass, which contains the residue of the silicates of the 'meteorite-magma', after a certain amount of it has crystallized as olivine or pyroxene, and this residual glass is even more readily soluble in acids than the crystallized olivine. Besides, when the plagioclase is more or less changed into maskelynite it becomes accordingly more or less readily attacked by the acid. The 'soluble portion' will therefore in certain chondrites contain appreciable amounts of other silicates than olivine silicates and it will not be possible to interpret it in terms of olivine silicates alone.

Further, it may be noted that the bulk analysis resulting from the summing up of the two partial analyses in most cases is less exact than when a single bulk analysis has been made of the silicate powder after the metallic portion has been dissolved out by special methods or determined in a separate portion of the powder.

Since the introduction of thin sections, and now that the microscopical-petrographical investigation of these has become the principal way of investigating stony meteorites as well as igneous rocks, it is probable that an approximate quantitative estimate of the amounts of olivine and pyroxene present in a chondrite can be made quite as well in thin section under the microscope as by the chemical method of dividing the material into an insoluble portion and one soluble in hydrochloric acid. The present author is therefore of the opinion that in most cases a single bulk analysis is preferable to the dividing up of the material into a portion soluble in acid and an insoluble portion. It should, however, be pointed out that in certain cases, as for instance the group of black chondrites and in stones containing much very fine-grained or dusty material, a microscopical determination of the character of the constituents cannot be made, and in such cases the chemical method of separation into a soluble and an insoluble portion is of value.

Examples could be given of a great many different ways in which the results of meteorite analyses have been published, but a discussion of

most of these methods seems of little interest and would occupy too much space. It is more practical to give here some examples of analyses of stony meteorites and to discuss in connexion with these examples the ways of stating the results of analyses and the interpretation of the analyses.

TABLE I. Chemical analyses of stony meteorites.

	1.	2.	3.	4.	1*a*.	2*a*.	3*a*.	4*a*.
SiO_2	34·82	39·39	36·55	38·47	39·07	46·55	47·57	59·84
TiO_2	0·15	0·13	0·14	0·12	0·17	0·16	0·18	0·18
Al_2O_3	2·18	2·64	1·91	1·78	2·45	3·11	2·18	2·77
Cr_2O_3	0·58	0·49	0·52	0·23	0·65	0·58	0·68	0·35
Fe_2O_3	—	—	—	—	—	—	—	—
FeO	24·34	14·13	10·21	0·23	27·30	16·71	13·29	0·35
NiO	—	—	—	0·11	—	—	—	—
MnO	0·20	0·28	0·35	0·02	0·22	0·33	0·42	0·03
MgO	23·57	24·21	23·47	21·63	26·44	28·60	30·54	33·64
CaO	2·17	1·82	2·41	1·03	2·43	2·15	3·14	1·60
Na_2O	0·69	1·09	0·78	0·64	0·78	1·29	1·01	1·00
K_2O	0·23	0·20	0·20	0·15	0·27	0·24	0·26	0·24
P_2O_5	0·20	0·24	0·30	tr.	0·22	0·28	0·39	—
H_2O+	0·10	—	0·15	0·34	—	—	—	
H_2O-	—	—	0·06		—	—	—	—
Silicate	89·23	84·62	77·05	64·75	100 %	100 %	100 %	100 %
					1*b*.	2*b*.	3*b*.	4*b*.
Fe	4·02	7·76	15·15	23·70	72·56	85·47	88·27	92·30
Ni	1·43	1·25	1·88	1·78	25·81	13·77	10·98	7·24
Co	0·09	0·07	0·13	0·12	1·63	0·76	0·75	0·46
Cu	—	—	—	—	—	—	—	—
Metal	5·54	9·08	17·16	25·60	100 %	100 %	100 %	100 %
Fe	3·25	3·88	3·88	5·07				
S	1·87	2·25	2·23	2·89				
Troilite	5·12	6·13	6·11	7·96				
C	0·07	—	—	0·32				
	99·96	99·83	100·29	99·91				

1. 'Ornansite', Warrenton, Missouri, U.S.A. Unpubl. analysis. H. B. Wiik analyst.

2. Average of twelve 'white chondrites'.

3. 'Crystalline chondrite', Oakley, Kansas, U.S.A. Unpubl. analysis. H. B. Wiik analyst.

4. 'Crystalline enstatite-chondrite', Daniel's Kuil, South Africa. G. T. Prior analyst. Total includes CaS 0·86 %, $FeCr_2S_4$ 0·42 %. (Ca = 0·48 %, Cr 0·22 %.) Total S = 3·51 %. C = 0·10 % according to Church, Chem. News, vol. 18 (1869), p. 258 [but 0·32 % acc. to Prior].

As an instance, an average of all the superior analyses of 'white chondrites', one of the largest 'natural groups' of chondrites, is given in

anal. 2–2*a*, table I. The analyses of the following white chondrites have been used in computing this average:

Tenham (Warbreccan), spring, 1879, analysed by G. T. Prior (4).
Grossliebenthal, 19.xi.1881, anal. P. Melikov and C. Schwalbe (5).
Perpeti, 14.v.1935, anal. E. Spencer and K. B. Sen (6).
Varpaisjärvi, found 1914, anal. H. B. Wiik (7).
Wittekrantz, 9.xii.1880, anal. G. T. Prior (8).
St. Cristophe, 5.xi.1841, anal. F. Pisani; see A. Lacroix (9).
St. Michel, 12.vii.1910, anal. L. H. Borgström (10).
Baroti, 5.ix.1910, anal. G. T. Prior (11).
Lanzenkirchen, 28.viii.1925, anal. E. Dittler (12).
Rangala, 29.xii.1937, anal. J. A. Dunn (13).
Narellan, 9.iv.1928, anal. T. Hodge-Smith (14).
Lundsgård, 3.iv.1889, anal. O. Nordenskiöld (15).

When occurring all Fe_2O_3 of these analyses has been calculated as FeO. H_2O has been left out in calculating this average composition. Nearly all the figures of these analyses vary only slightly from the corresponding figures of the average 2, table I.

Water, Fe_2O_3, and NiO as determined in the analyses are given in the statement of the analytical results 1, 3, and 4, table I. Water and Fe_2O_3 if occurring in considerable amount indicate that the stone is much altered by weathering as is the case with many stony meteorites ploughed up from the soil years after they have fallen. NiO together with Fe_2O_3 and H_2O in an analysis indicates a far-reaching decomposition of the nickel-iron of the stone. In stony meteorites which are not decomposed NiO in an analysis indicates that the magnetic separation of nickel-iron has not been complete and that some nickel-iron has remained in the material used for the analysis of the silicate portion.

Although analysis 2 in table I represents fairly well also the average chondrite, since most of the intermediate chondrites, the grey chondrites, and many of the spherical chondrites are of chemical compositions not differing much from that of the white chondrites, the variation in chemical composition of the chondrites is fairly wide. For comparison, therefore, analyses are here given of representatives of the group of chondrites with the lowest amount of silica, anal. 1, table I, the ornansite of Warrenton and of the group of chondrites with the highest amount of silica, the crystalline enstatite-oligoclase chondrite of Daniel's Kuil, anal. 4, table I. The ornansites have not only the lowest contents of silica among the chondrites, but also the lowest contents of metallic nickel-iron and the highest contents of ferrous silicate and ortho-silicates. The crystalline enstatite-chondrites have the highest amounts of silica, of metallic nickel-iron, and of metasilicates, and the lowest amount of

ferrous silicates. All the other chondrites vary in composition between the ornansites and the enstatite-chondrites of the Hvittis-type to which Daniel's Kuil belongs. In addition, as an example of the chondrites rich in nickel-iron, the crystalline chondrite of Oakley is given as anal. 3 of table I. These four analyses in table I are thus fairly well suited to illustrate here the statement of analytical results with regard to chondrites.

In the following calculations the H_2O of analyses 1, 3, and 4 has been left out as not forming an original constituent of the meteorites. Fe_2O_3 occurring in small amounts in some of the analyses of the 'white chondrites' has been —as mentioned above—calculated as FeO. Small amounts of NiO, calculated as Ni, may, together with an amount of FeO corresponding to the proportion between Ni and Fe in the metallic portion, the FeO calculated as Fe, be added to the nickel-iron. Rare elements in small amounts determined in the analysis are preferably not included in the table but are mentioned in the text after the locality and name of the analyst. Here also the figures for the rare sulphides occurring in some stony meteorites, for instance in Daniel's Kuil, anal. 4, table I, may be given in detail.

In order to facilitate calculations and comparisons table I has been divided horizontally in such a way that the silicate portion, the metallic portion, and the sulphide portion of the meteorite are each summed up separately. In this way a comparison between the relative amounts of silicate, metal, and sulphide in different kinds of meteorites is facilitated, a comparison which is of importance also with regard to the possible occurrence of distinct silicate, sulphide, and metal shells in the body of the earth.

In cases where the amount of nickel-iron varies as much as in these four analyses in table I it is of interest to compare the composition of the silicate portions of the chondrites. Therefore the silicate portions of the four analyses, as calculated to 100 %, are given in 1*a*, 2*a*, 3*a*, and 4*a*, table I; also the nickel-iron portions as calculated to 100 % are given in 1*b*, 2*b*, 3*b*, and 4*b*.

The variation in composition of the silicate portions of stony meteorites is more distinctly seen from these analyses 1*a*–4*a* than from the bulk analyses 1–4. Especially the big difference in SiO_2 content between the different 'natural groups' of chondrites is well shown. We see further that MgO increases in proportion to the increase in the SiO_2, although much less than SiO_2. With the rise of SiO_2 the amount of FeO falls, becoming zero in the group of 'crystalline enstatite chondrites'. This

decrease in FeO is of course a result of the simultaneous and corresponding increase of metallic iron as seen from the analyses 1 to 4, table I. We see further from the analyses 1*a*–4*a*, table I, that while MgO increases with SiO_2 and FeO decreases, the other chemical components are not affected by this change, but remain fairly constant in all groups of chondrites.

The variation in the composition of the metallic nickel-iron in the different natural groups of chondrites is seen from the analyses 1*b*–4*b*, table I, as well as from the bulk analyses 1–4. We see clearly that with the decrease in the amount of nickel-iron, the nickel amount increases very considerably, as pointed out earlier by Prior (16).

In a previous paper on the chemistry of the meteorites (17) the present author pointed out that if the bulk analyses are calculated as free of oxygen and the metal atoms to 100 %, one finds that the difference in the metal atom composition of the several kinds of chondrites is but small. It was also pointed out that the difference in chemical and mineralogical composition of the different types of chondrites is therefore in reality a case of a different degree of oxidation. The proportion between all the metal atoms taken together and the number of the oxygen atoms present in a meteorite is a measure of the degree of oxidation of the meteorite and is an important means of comparison of meteorites amongst themselves and of meteorites with terrestrial rocks, which are to a much higher degree oxidized than the meteorites containing metallic nickel-iron. Such a comparison is, however, beyond the scope of this paper and will be dealt with in a separate publication.

Calculation of the mineral composition of stony meteorites from the analytical results.

Just as the analytical results have been published in many different ways—and not always in such a way as to allow of a bulk analysis of the meteorite being derived from the figures given—also the calculation of the mineral composition from the analytical results has been given in many different ways. As is well known, the calculation of the mineral composition of an igneous rock from the analysis is a complicated matter and has led to the introduction by American petrographers of a 'norm' calculation. Farrington tried to introduce a similar quantitative classification for stony meteorites (18), but his attempt cannot be regarded as successful, mostly on account of the small number of sufficiently accurate chemical analyses available at the time of his

publication, and also because Farrington in his calculations used a great number of inferior analyses.

On account of the non-existence in meteorites of the complicated silicates of the mica- and hornblende-groups, a calculation of the mineral composition of a stony meteorite is less complicated than the calculation of the 'mode' of an igneous rock. In most cases a kind of 'norm' of a meteorite, which at least approximately corresponds to its 'mode' or actual mineralogical composition, can be calculated from the analysis. In table II such examples are given of the calculation of the mineral composition from analyses 1, 2, 3 and 4, table I.

TABLE II. Mineral 'norms'.

	1.	2.	3.	4.
$Na_2O.Al_2O_3.6SiO_2$ ...	5·11	8·38	5·50	5·27
$K_2O.Al_2O_3.6SiO_2$ ...	1·34	1·16	1·16	0·89
$CaO.Al_2O_3.2SiO_2$ ...	2·55	2·20	1·69	1·53
$FeO.SiO_2$	0·12	7·36	6·31	0·03
$FeO.TiO_2$	0·28	0·24	0·33	0·23
$MnO.SiO_2$	0·37	0·51	0·45	0·04
$CaO.SiO_2$	2·94	2·26	3·58	2·21
$MgO.SiO_2$	0·16	16·50	20·63	53·85
$2FeO.SiO_2$	33·91	13·85	8·95	—
$2MgO.SiO_2$	41·12	30·67	26·47	—
$FeO.Cr_2O_3$	0·85	0·71	0·76	0·33
$3CaO.Na_2O.P_2O_5$ ...	0·52	0·63	0·79	—
SiO_2	—	—	—	0·34
Fe	4·02	7·76	15·15	23·70
Ni	1·43	1·25	1·88	1·78
Co	0·09	0·07	0·13	0·12
FeS	5·12	6·97	6·11	8·09
CaS	—	—	—	0·86
$FeCr_2S_4$	—	—	—	0·40
C	0·07	—	—	0·10
	100·00	100·52	99·89	99·77

TABLE II*a*.

	1.	2.	3.	4.
Felspars	9·00	11·70	8·35	7·69
Pyroxenes	3·85	26·87	31·30	56·36
Olivine	75·03	44·52	35·42	—
Chromite	0·85	0·71	0·76	0·34
Merrillite	0·52	0·63	0·79	—
Quartz	—	—	—	0·34
Nickel-iron	5·54	9·08	17·16	25·60
Troilite	5·12	6·97	6·11	8·09
Oldhamite	—	—	—	0·86
Daubréelite	—	—	—	0·40
Carbon	0·07	—	—	0·10
	99·98	100·48	99·89	99·78

In these calculations the following rules have been followed:

1. After the molecular proportions have been ascertained in the usual way an amount of Na_2O and CaO necessary to bind all the P_2O_5 of the analysis as merrillite, $3CaO.Na_2O.P_2O_5$, is deducted from the bulk of CaO and Na_2O.

2. The remaining Na_2O is combined with the corresponding amount of Al_2O_3 and SiO_2 to form the albite molecule. All K_2O is combined with Al_2O_3 and SiO_2 to form the orthoclase molecule. The remaining Al_2O_3 is combined with a corresponding amount of CaO and SiO_2 to form anorthite. In this way the amount of felspar (and maskelynite) silicates, crystallized as well as contained in the glassy portion of the chondrules and of the meteorites, is determined by the analytical figure for Al_2O_3. It is therefore necessary that TiO_2, Cr_2O_3, MnO, and P_2O_5 be determined in the analysis, otherwise an omission of the determination of one or more of these minor constituents will lead to too high a figure for Al_2O_3 and too high an amount of anorthite with a correspondingly too low figure for the pyroxene component $CaSiO_3$.

3. If the stone contains oldhamite, CaS, a corresponding amount of calcium is obtained in solution after digesting a portion of the powder in water slightly acidified with acetic acid. After deducting an amount of CaO corresponding to the oldhamite, any remaining CaO is combined with SiO_2 to form $CaSiO_3$ which is counted as belonging to the pyroxenes of the meteorite.

4. TiO_2 is combined with FeO to form $FeTiO_3$, which is added to the pyroxene silicates replacing $FeSiO_3$. Ilmenite has so far not been proved to occur in stony meteorites. Titanium, however, is possibly present as Ti_2O_3 in the pyroxenes, and admittedly the whole question of how the titanium occurs has to be solved by future research.

5. Cr_2O_3 is combined with FeO to form chromite $FeCr_2O_4$, except in stones like Daniel's Kuil, anal. 4, table I, where part of the Cr_2O_3 occurs in the soluble portion of the meteorite. In such a case this portion of the Cr_2O_3 should be calculated as daubréelite, $FeCr_2S_4$.

6. All Fe_2O_3 of the analyses is calculated as FeO and added to the quantity of FeO found, since it is very uncertain whether any magnetite occurs, or theoretically could at all exist in a chondrite containing metallic nickel-iron. The only instances where one could expect to find magnetite or where magnetite has been reported to occur seem to be in the almost totally oxidized achondrites which do not contain any metallic nickel-iron. But this problem also has to be clarified by further research.

All MgO and FeO are combined with SiO_2 to form $MgSiO_3$, Mg_2SiO_4, $FeSiO_3$, and Fe_2SiO_4, the proportion of metasilicates to orthosilicates being calculated in the same way as in the 'Quantitative classification of igneous rocks' (1), p. 193, paragr. 18a, to p. 199.

This calculation based on the proportion between available SiO_2 molecules and FeO+MnO+MgO molecules gives us the proportion between the FeO and MgO metasilicates contained in the pyroxenes and FeO and MgO orthosilicates contained in the olivine, and thus, if $FeTiO_3$ and $CaSiO_3$ are added to the $FeSiO_3$ and $MgSiO_3$ pyroxene silicates, the proportion between pyroxenes and olivine contained in the stone. However, in this norm calculation the Mg and Fe silicates are allotted to the pyroxene and the olivine in the same proportion and do not give any information as to the actual distribution of iron and magnesia silicates in these minerals. From investigations on achondrites we know that the proportions between FeO and MgO are not the same in pyroxenes and olivines contained in the same stone, and where these minerals have crystallized from a melt we must expect that the proportions between FeO and MgO will be different in the two mineral series. The actual equilibrium conditions, however, are not known, but further studies of certain of the achondrites may throw light on these interesting relations concerning the distribution of FeO and MgO silicates between the pyroxenes and the olivines. Where optical determinations on achondrites are possible the results can be used in calculating the 'norm' and thus include a calculation of the actual proportions of the FeO and MgO silicates contained in the pyroxenes and olivines. In the chondrites conditions are more complicated and it seems that in many stones both enstatite chondrules and bronzite and hypersthene chondrules occur, while the olivines of different chondrules may perhaps also have a different composition; but these questions need further investigation. Prior has proposed to designate the ratio MgO : FeO in the silicate portion of a stony meteorite by m and the ratio of percentage weight of Fe : Ni in the metallic portion of the stones by n.

The figures of a table of mineral constituents such as table II are, however, greatly influenced by the quality of the analyses and especially by the exactness of the determination of the amount of metallic nickel-iron present, and the proportion between metallic iron and FeO, which is the most difficult determination in the analyses of stony meteorites and siderolites.

A similar way of calculating the mineral composition of the Suwahib meteorite has been used by Campbell Smith (19) and modifications of

such methods have been used by Prior and also by some other authors. Were the 'rules' according to which the mineral compositions in table II have been calculated to be generally accepted, we would obtain 'norms' which probably would be very close to the actual mineralogical composition and could better serve as a basis for petrological comparison than some of the earlier methods of calculating the mineral composition which in some points vary amongst themselves.

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Mineralogical applications of a two-crystal Weissenberg X-ray goniometer

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Introduction.

THE study of minerals, using X-ray goniometers in place of optical instruments, has proceeded far in recent years. It is now a common practice among mineralogists and petrologists to confirm the nature of a given specimen by X-ray methods when there is some doubt about the identification by the older methods. The occurrence of pseudomorphs sometimes leads to misidentifications even in crystals of large size. If the material is cryptocrystalline it may be almost impossible to make an identification by optical methods. In such cases X-ray photographs may be of great assistance. When the atomic arrangement is simple, giving a powder photograph that has only a few lines, the identification can be carried out by using standard indexes of powder photographs or, often more simply, by comparing the photograph of the unknown mineral with those of likely known minerals. If the mineral to be identified occurs in single crystals it is usually better not to take powder, but rather single-crystal, photographs. From such photographs the cell dimensions, axial ratios and angles, and most of the symmetry elements may be found. Many minerals are solid solutions and the cell dimensions change with the composition. A measurement of the cell dimensions may enable the composition to be determined. For such measurements, however, high accuracy is required; special types of goniometer and methods of using them have been developed for the purpose.

The distribution of atoms within the unit cells of many minerals is now well known and much research is directed to completing this branch of mineralogy. For such studies a number of experimental techniques have been devised, mostly depending at some stage on accurate information concerning the intensity of X-ray reflections from particular atomic planes. For this purpose oscillation or Weissenberg photographs have been extensively used, though ionization- or counter-spectrometers have also proved of value. The measurement of the intensity of a particular X-ray reflection is beset with two difficulties.

One concerns the crystal itself and the other the recording apparatus. In order that the measurement shall have significance the conditions under which the reflection occurs must be strictly defined. For example, according to one method, the reflecting surface must be flat and large enough to intercept the whole X-ray beam. Alternatively the crystal must be so small that it is completely bathed in the X-ray beam and, at the same time, it must be so weakly absorbing that the X-rays can pass through it with less than about 30 % reduction in intensity. The recording apparatus must satisfy the requirement that all X-ray reflections from planes on a given crystal must have the same chance of registering their intensity. For this purpose the X-ray beam must be constant in intensity and the photographic film must be equally sensitive for each crystal reflection. These requirements are not easily met and it is especially difficult when the reflections which have to be compared come from different crystals. It was in connexion with this problem that the present instrument was originally devised. (Wooster, 1948.)

The chemical analysis of minerals has been carried out for many years, but constant efforts are made to reduce the labour and the time required for performing such analyses. Spectrographic and other techniques can be employed to determine the presence or amount of certain elements with greater ease than the older methods. A method, as yet little used, based on the differences of absorption of X-rays by the chemical elements can also be employed. This is unlikely to be used except for a limited number of elements, but as these include many of the common metals the method may prove important. The instrument described below is well suited for this kind of determination of X-ray absorption coefficient.

General description of the apparatus.

The Weissenberg type of X-ray goniometer provides for simultaneous rotation of the crystal and translation of the camera. The X-ray beam, usually horizontal, falls on a crystal oscillating about a horizontal axis perpendicular, or nearly perpendicular, to the X-ray beam. The cylindrical camera is coaxial with the axis of oscillation of the crystal and moves in a direction parallel to that axis. In fig. 1 there is a general view of the apparatus. The X-ray beam enters from the back through a horizontal cylindrical aperture, and after striking the crystal falls upon the objective of the tele-microscope.[1] The horizontal axis on which both crystals are mounted runs from left to right and intersects the axis

[1] A microscope that can be used as a telescope.

of the telescope. The two goniometer heads can just be seen pointing towards one another in fig. 1. When every adjustment has been made the two crystals are 3 mm. apart. The cylindrical camera is constructed

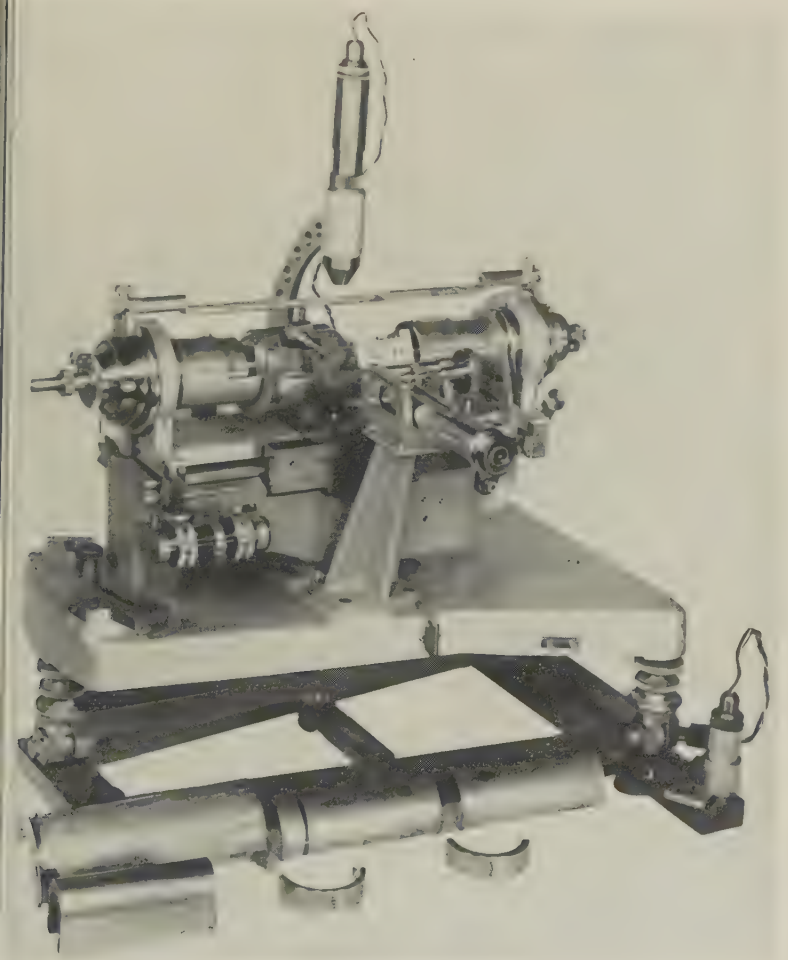

FIG. 1. Genera lview of the two-crystal Weissenberg goniometer.

from two hemicylinders since it is not possible to have two crystals mounted 3 mm. apart and place around them a whole cylinder. In fig. 1 the lower half of the camera can be seen in its usual place on the instrument and the upper half is lying in front of the base. The camera is

mounted on a carriage similar to that of the moving roller on many typewriters. This carriage has two V-grooves which are opposite corresponding V-grooves on the track. Ball-bearings between these V-grooves enable the carriage to move freely from left to right and back again. Under the track there is visible in fig. 1 a box which contains the synchronous driving motor. The motor rotates a worm long enough to move the camera through 10 cm. by means of a nut riding on the screw thread. A steel tape is attached to one end of the camera carriage and passes over a small pulley to a cylindrical drum on the right-hand end of the crystal axis. This tape is kept taut by a second tape attached to the same drum at one end and to a spring-box at the other. In this way a uniform movement of the camera and the crystal can be obtained and while the crystal turns through 200° the camera moves along 100 mm. At each end of the sideways movement of the camera the motor is reversed, simply by stopping it. As the motor is synchronous it can rotate equally well in either direction and if stopped from going in one direction it reverses and rotates in the opposite direction (Wooster, 1948). The left-hand goniometer head is rotated by means of a bar which can be rigidly clamped to both goniometer heads. This is shown at the top of the instrument in fig. 1. The goniometer heads are mounted on a frame which, like the camera carriage, can move along the track on ball-bearings; the extent of its movement never exceeds 5 mm. and between its resting positions is a distance of 3 mm. A toothed-wheel mechanism (see fig. 2) is automatically operated every time the camera carriage reaches the right-hand side and this exchanges the crystal which is in the X-ray beam with the one which previously was 3 mm. to one side of the beam. The box under the track is pivoted about a vertical axis running through the base of the instrument, so that, without altering the position of the collimator relative to the X-ray tube, equi-inclination Weissenberg photographs may be taken. The maximum possible angle of rotation of the base is $\pm 20°$. Since it is essential in taking Weissenberg photographs that only one layer line should be recorded on any photograph, all unwanted reflections are excluded by cylindrical screens with circumferential slots. These are necessarily in the form of hemi-cylinders which, when placed in position on the instrument, form cylinders coaxial with the camera. The lower halves are shown in place on the instrument in fig. 1 and the upper halves are lying in front of the base. The right-hand screens are attached to a cylinder which does not move when the goniometer heads move sideways. The left-hand screens move with the goniometer heads,

sliding outside the right-hand screens. Thus it can be arranged that when the right-hand crystal is in the beam, X-rays which have been reflected through both the upper and lower hemi-cylindrical screens can reach the film, whereas when the left-hand crystal is in the beam, the lower or the upper opening in the screen is closed while the other one is open. The crystals are accurately set by taking an oscillation photograph. For this purpose the cylindrical screens are moved sideways from the centre, leaving a free space. Only the upper half of the

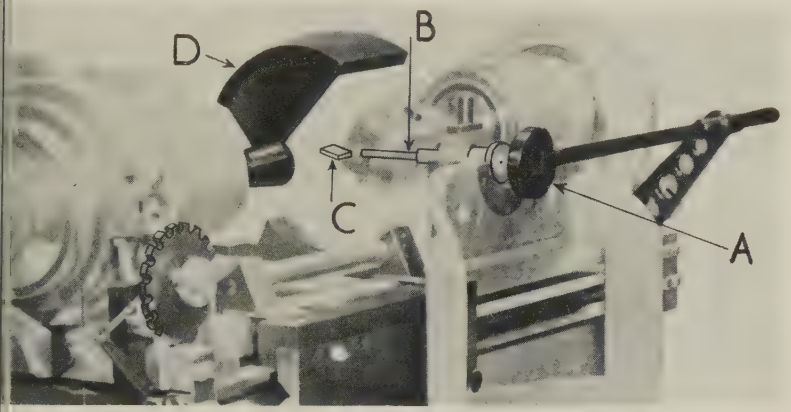

FIG. 2. Photograph of two-crystal Weissenberg goniometer arranged for the measurement of absorption coefficients. A, holder for absorbers; B, collimator; C, monochromatizing crystal; D, camera.

camera is used, and this is mounted by means of two special spacing-rings on the screens so that it is co-axial with the axis of oscillation of the crystal. The base of the instrument has three levelling toes which rest in a frame provided with the usual conical depression, groove, and plane for the three toes. This frame is mounted on three wheels which enable the instrument to be moved towards, or away from, the X-ray tube with ease. The wheels run on a T-shaped frame and by means of a clamp the instrument may be fixed in any desired position relative to this frame.

Applications of the two-crystal method.

1. *The comparison of the intensities of reflection of particular planes in one crystal with those of particular planes of a standard crystal.*

It is usual in the determination of a crystal structure to require a knowledge of the absolute structure amplitudes, F_{hkl}, of at least a

certain number of reflecting planes. These structure amplitudes are connected with the atomic parameters of each of N atoms by the formula

$$F_{hkl} = \sum_{n=1}^{n=N} f_n \cos 2\pi(hx_n+ky_n+lz_n)$$

when a centre of symmetry is at the origin of the co-ordinate system. In the absence of such a centre of symmetry the formula is more complicated but the physical principles involved are the same. In this formula

N = number of atoms per unit cell,

f_n = atomic structure factor for the nth atom,

x_n, y_n, z_n = co-ordinates of the nth atom,

h, k, l = indices of the reflecting plane.

The simplest application of this method arises when $N = 2$. Then,

$$F_{hkl} = 2f \cos 2\pi(hx+ky+lz),$$

and from three values of F_{hkl}, obtained by the study of only three reflections, x, y, z can be determined. In principle, therefore, an absolute measurement of F_{hkl} leads to a direct determination of the atomic co-ordinates, when the structure is simple. When the structure is more complicated various combinations of experimental observations are employed to determine x_n, y_n, z_n for all values of n. Some of these methods depend on a determination of *relative* values of F_{hkl}, which can most conveniently be obtained from a Weissenberg photograph, while others require *absolute* values of F_{hkl}. The absolute value of F_{hkl} can be obtained by finding the ratio of the intensity of the reflection from the particular plane hkl to the intensity of the direct beam. Account must, of course, be taken of the fact that the crystal reflects over a certain range of angle and not only at a particular setting. It is difficult to make such an absolute measurement because the direct beam is usually not strictly monochromatic and any direct beam will produce a much greater effect on a photographic film than corresponds to its monochromatic component. To overcome this difficulty it is usual to calibrate the intensity of the direct beam by reflecting it from a crystal of known reflecting power. This method, however, introduces its own difficulties. If the X-ray beam is reflected from the standard crystal at a different time from that during which it is reflected from the crystal under examination, the intensity of the incident beam may not be the same during the two reflections. The mains voltage and frequency are always fluctuating, so that the maintenance of an X-ray beam of sufficient constancy is almost impossible over periods during

which X-ray photographs are taken. It therefore becomes necessary to interchange the two crystals in the X-ray beam a large number of times during the exposure if a sufficiently accurate comparison is to be made.

A further difficulty arises in registering the intensity of two reflected beams with equal sensitivity. If the records are made on separate pieces of photographic film, it is difficult to avoid errors due to differences in development and processing generally. These difficulties can be overcome only by recording the two beams, one from the standard crystal and the other from the crystal under examination, on the same piece of film. Thus the two essentials of a satisfactory instrument for the determination of absolute values of F_{hkl} are (1) a frequent exchange in the X-ray beam of the two crystals and (2) the record of both reflections shall be made on the same film, in such a way that they are clearly distinguished from one another. The instrument described here satisfies both these conditions. Two experiments are described below, both illustrating applications of the two-crystal goniometer to the problem of comparing the intensities of reflection from a standard crystal and another crystal.

1.1 *Comparison of the integrated reflections of the h*00 *reflections of calcite and rock-salt.* As mentioned above, in one type of measurement a plate of crystal is used which intercepts the whole X-ray beam. The integrated reflection, obtained by recording all the radiation reflected as the crystal rotates at a uniform speed through the reflecting setting, is, under this experimental condition, easily related to F_{hkl}. In the following experiment a cleavage plate of rock-salt was mounted on one goniometer head and a cleavage plate of calcite on the other goniometer head. By manually controlling the movement of the toothed wheel the ratio of the number of times that the rock-salt and calcite crystals came into the beam was 1 : 6, 1 : 5, 1 : 4 in the three photographs of fig. 3 (reading left to right). The strongest reflections are 200 for rock-salt and 100 for calcite (unit cell of same shape as the cleavage rhombohedron). It will be seen that these spots are most nearly equal for the middle photograph where the ratio of exposures was 1 : 5. Thus it is possible to see directly that for these particular crystals of rock-salt and calcite the ratio of the integrated reflections was 5 : 1. A more accurate comparison could be made by using a micro-photometer to determine the total blackening of the spots. This method could be applied to the comparison of any series of reflections arising from the first, second, &c., orders of reflection from a plane parallel to the surface of the crystalline plate. The second experiment is directed to showing

how the instrument may be used for determining the absolute values of a series of reflections from planes having indices such as *hko*, *okl*, or *hol*.

1.2. *The determination of the integrated reflections for a number of planes having a common zone axis.* Most minerals have crystal structures with many parameters and a number of methods have been devised for finding the atomic distribution. One of these depends on a knowledge of the absolute values of F_{hko}, F_{okl}, and F_{hol}, i.e. on the structure ampli-

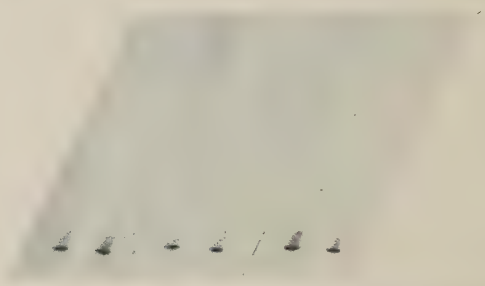

FIG. 3. Portions of three two-crystal Weissenberg photographs comparing the intensities of reflection of rock-salt (left) and calcite (right) in each photograph.

Left-hand photograph	Exposure of	rock-salt 1
	,,	,, calcite 6
Middle photograph	,,	,, rock-salt 1
	,,	,, calcite 5
Right-hand photograph	,,	,, rock-salt 1
	,,	,, calcite 4.

tudes of planes parallel respectively to the crystallographic z, x, and y axes. A Weissenberg photograph of one crystal set up with the appropriate orientation can provide *relative* values of F_{hko}, but to obtain *absolute* values it is necessary to calibrate the intensity of the incident beam by using two crystals. It is always best to use a standard crystal of somewhat similar chemical and physical character to the crystal under examination. Quartz is therefore a suitable standard for silicate minerals, and in the photograph of fig. 4 quartz is the standard with which natrolite is compared. The crystals used for obtaining the photographs of fig. 4 were needles approximately 0·3 mm. in diameter and 3 mm. long. For accurate work the crystals must be carefully measured to determine the effect of absorption of X-rays in the specimen and also the effect of the actual shape in favouring certain reflections at the expense of others. The lower half of the photograph records the reflections from the natrolite only while the upper half has these reflections and those of the quartz crystal as well. With care it is easy to distinguish

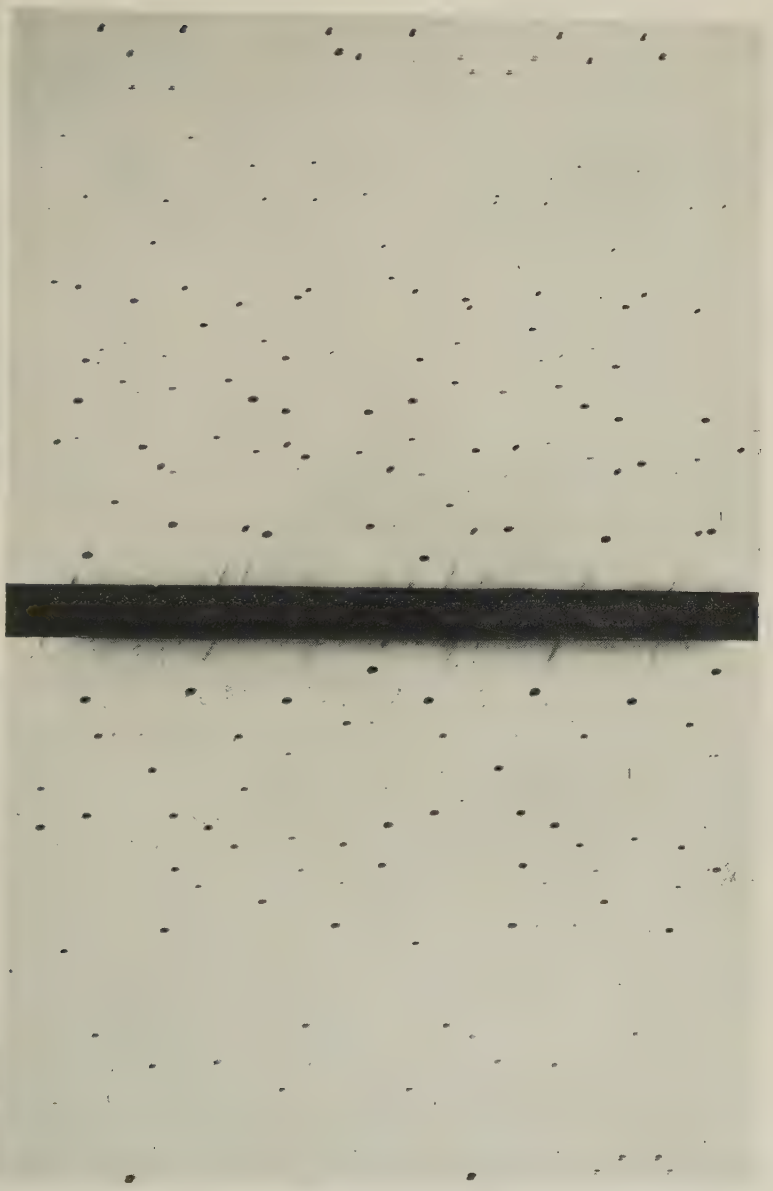

FIG. 4. Two-crystal Weissenberg photograph using Cu-$K\alpha$ and radiation filtered through nickel. *Upper half*: quartz rotation axis [001], superimposed on natrolite rotation axis [001]. *Lower half*: natrolite alone.

between the reflections from the two crystals because the position of the natrolite spots in the upper half can be derived from the position of the corresponding spots in the lower half. In taking this photograph each crystal remained in the X-ray beam for an equal length of time and, during the several hours' exposure, each crystal was moved into and out of the beam some 30 times. Thus any variations in the intensity of the X-ray beam are likely to be of small influence on the accuracy of the comparison between the intensities of reflection from the two crystals. Much valuable work can be done by simple visual comparison of the spots produced by the natrolite with those produced by the quartz, but for accurate work it is necessary to determine the total blackening of the spots with an integrating micro-photometer. The particular crystal of quartz which is used as a standard can be directly calibrated on an ionization- or counter-spectrometer. Any or all of the reflections recorded on the photograph can be registered by a counter spectrometer from the same small crystal using strictly monochromatic radiation. The intensity of the direct beam can be measured immediately before and after the measurement of each integrated reflection. In this way no assumptions need be made about the perfection, or absorption of the standard crystal.

2. *An X-ray method of determining the amount of a particular element in the composition of a mineral.*

2.1. *General principles.* When X-rays pass through any crystal the absorption is determined, except under certain special circumstances, by the number and kinds of atoms passed through and not at all by their arrangement. The special circumstances referred to arise only when a strictly parallel monochromatic beam is employed and an appreciable fraction of the beam is reflected by a set of atomic planes. Usually if in passing through a thickness, t, of a crystal the intensity of the X-rays is reduced from I_0 to I, then

$$I = I_0 e^{-\mu t}, \tag{1}$$

where μ is the linear absorption coefficient.

An absorption coefficient which is of importance in connexion with minerals is the gram-atomic absorption coefficient, μ_g, since this is readily applicable when the composition is expressed in percentages of metallic oxides. The relation between μ and μ_g is defined by the expression

$$\mu_g = W\mu/\rho \quad \text{or} \quad \mu = \rho\mu_g/W,$$

where W = atomic weight, ρ = specific gravity.

In a compound containing m types of atoms, each formula weight containing n % of atoms of each type, the value of μ is given by

$$\mu = \rho \sum^{m} n\mu_g \Big/ \sum^{m} nW. \qquad (2)$$

This formula is valid because, as mentioned above, the absorption effects of different atoms are additive.

The variation of μ_g for Cu-$K\alpha$ radiation ($\lambda = 1{\cdot}54$ Å.) with atomic number of the absorbing element is large, as is shown in Fig. 5. The

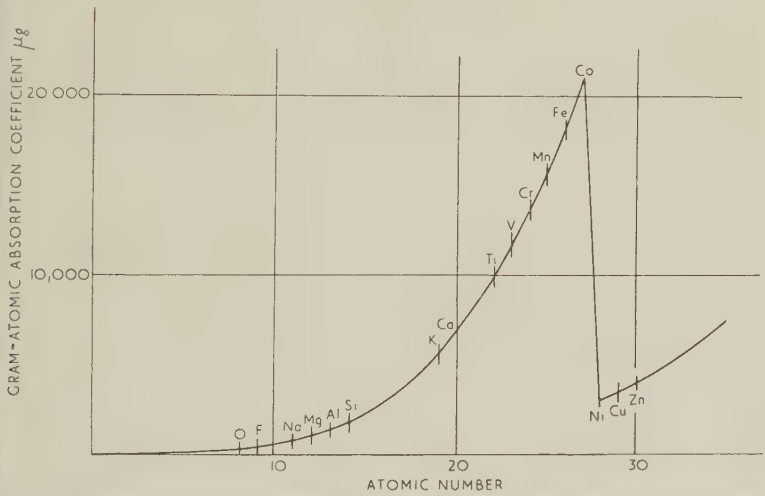

FIG. 5. Diagram showing variation of gram-atomic absorption coefficient with atomic number.

maximum value for the characteristic $K\alpha$ radiation of copper is that of cobalt which is 20,900. Iron is close to this, being 18,100. Among the elements commonly occurring in minerals calcium and potassium are next in order, having coefficients of 6,890 and 5,590 respectively. The elements Si, Al, Mg, Na, F, and O have small absorption coefficients, all being less than 2,000. Thus in minerals containing one of the transition metals between titanium and cobalt the effect of x % of the transition metal is approximately the same as that of $10x$ % of the elements Na, Mg, Al, and Si. Thus the fraction of the mineral consisting of iron exercises a preponderating influence in determining the absorption

coefficient. If the characteristic radiation of nickel ($\lambda = 1{\cdot}66$ Å.) were used, iron would have the greatest absorption coefficient. Similarly with cobalt radiation ($\lambda = 1{\cdot}79$ Å.), the corresponding element is manganese and with chromium radiation ($\lambda = 2{\cdot}29$ Å.) the most heavily absorbing element is titanium. Thus to each characteristic radiation there corresponds a small group of elements which have a preponderating influence on the absorption coefficient. In the following section this general relation between absorption coefficients and chemical composition is applied to an isomorphous series of iron-containing minerals, namely, the micas.

2.2. *Relation between linear absorption coefficient and chemical composition in the micas.* The micas form a series of minerals in which the iron content ranges from very little to almost 30 %. The variation of the absorption coefficient for copper radiation over the whole series is, therefore, large. To illustrate the method of calculating the absorption coefficient, the biotites listed on p. 630 of Dana's 'Descriptive Mineralogy' (1892) and a few other micas are here chosen. The percentage composition of no.1 on p.630 is given as follows: SiO_2 40·00, Al_2O_3 17·28, Fe_2O_3 0·72, FeO 4·88, MgO 23·91, K_2O 8·57, Na_2O 1·47, H_2O 1·37, F 1·57. The gram-atomic absorption coefficients, μ_g, of the oxides can be readily obtained from the atomic weights and mass absorption coefficients (International Tables for Crystal Structure Determination (1944)). Thus for SiO_2 we have

$$\mu_g = 1690 + 2 \times 203 = 2{,}096$$

and the corresponding figures for the other oxides are Al_2O_3 3,229, Fe_2O_3 36,809, FeO 18,303, MgO 1,191, K_2O 11,383, Na_2O 1,625, H_2O 203, F 332. To apply formula (2) the percentage composition is multiplied by the gram-atomic absorption coefficient for each oxide and the sum of these products taken ($\sum^{m} n\mu_g$). The percentage composition is multiplied by the molar weight of each oxide in turn and the sum taken ($\sum^{m} nW$). The ratio of these two quantities, multiplied by the density, gives the linear absorption coefficient μ. Thus, in this example, for which the density is 2·87, μ is 169 cm.$^{-1}$* This computation was carried

* $\frac{\mu}{2{\cdot}87} = (40{\cdot}00 \times 2096 + 17{\cdot}28 \times 3229 + 0{\cdot}72 \times 36{,}809 + 4{\cdot}88 \times 18{,}303 + 23{\cdot}91 \times 1{,}191 + 8{\cdot}57 \times 11{,}383 + 1{\cdot}47 \times 1{,}625 + 1{\cdot}37 \times 203 + 1{\cdot}57 \times 332)/(40{\cdot}00 \times 60 + 17{\cdot}28 \times 102 + + 0{\cdot}72 \times 160 + 4{\cdot}88 \times 72 + 23{\cdot}91 \times 40 + 8{\cdot}57 \times 94 + 1{\cdot}47 \times 62 + 1{\cdot}37 \times 18 + 1{\cdot}57 \times 19)$

or, finally

$$\mu = 169 \text{ cm.}^{-1}.$$

ut for each member of the series of micas on p. 630 of Dana's 'Descrip-ive Mineralogy' for which the density was given and some phlogopites nd muscovites as well. To compare the absorption coefficient with the ercentage of iron in the mineral it is necessary to bring Fe_2O_3 and FeO

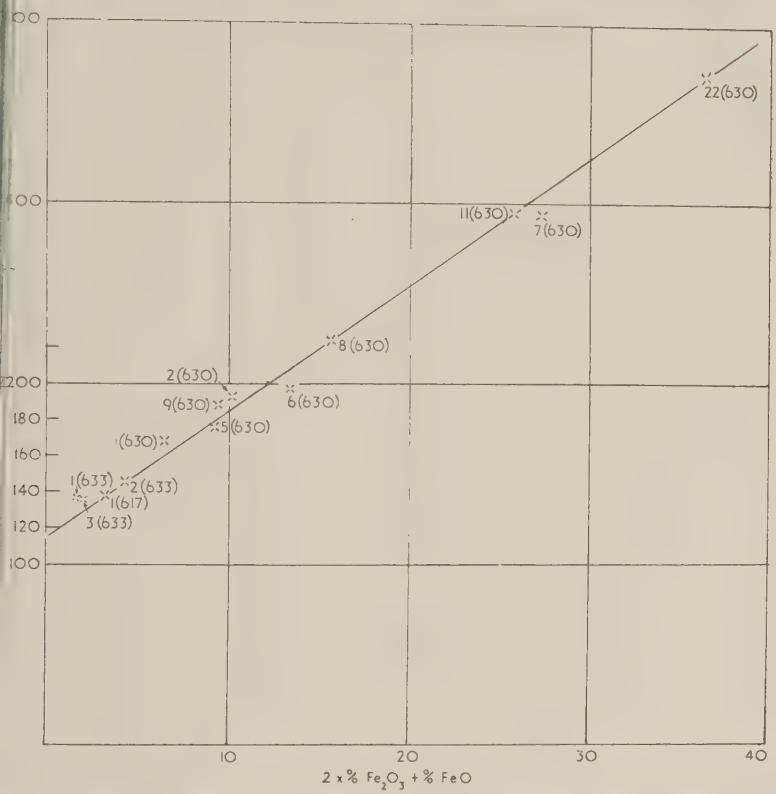

Fig. 6. Diagram showing the variation of linear absorption coefficient with percentage of iron in various micas.

on to a comparable basis. The gram-atomic absorption coefficient for Fe_2O_3, 36,809, is almost twice as great as that of FeO, 18,303, and we may therefore regard one molar weight of Fe_2O_3 as twice as absorbing as one molar weight of FeO. Thus, in the graph of fig. 6, the linear absorption coefficient μ, has been plotted against $(2\times\%\ Fe_2O_3 + \%\ FeO)$. A straight line has been drawn through the points corresponding to the various micas. It is significant that the line is straight, indicating that the iron content alone determines the change in absorption coefficient.

It is also important that the maximum horizontal deviation of the points from the straight line corresponds to just over 1 % of FeO. The accuracy of analysis of the iron-content is unknown, but it is clear that the absorption coefficient could be used in conjunction with this graph to determine the percentage of iron oxide in any of the micas listed here with an accuracy of about ± 1 %.

From this example it is possible to see which mineral groups lend themselves to partial chemical analysis in this way. The necessary conditions are as follows: (*a*) a concentration of FeO amounting to a few per cent., (*b*) the absence of a large amount of titanium, calcium, or potassium, unless a constant percentage of these elements is present throughout the series. If the percentage composition of titanium is being studied, then similar conditions can be laid down. Bearing these limitations in mind, the following mineral series are probably suitable for study: pyroxene, amphibole, garnet, chrysolite, tephroite (for manganese), humite, tourmaline, staurolite, mica, and serpentine. In each series it is to be expected that if a measurement of the absorption coefficient can be made accurate to x %, then the percentage composition of the iron or titanium or manganese can be found with an accuracy of $(x+y)$ %, where y depends on the deviations from the straight line in the graph of absorption coefficient plotted against percentage composition of the heavily absorbing element. In the case of the micas y appears to be about ± 1.

2.3. *The experimental measurement of the linear absorption coefficient using the two-crystal Weissenberg goniometer.* The measurement of a linear absorption coefficient involves a determination of the thickness, t, of the material traversed by the X-rays and the ratio of the intensity of the X-rays after passing through, I, to that of the X-rays at incidence, I_0. The equation (1) may be written

$$\mu = \frac{1}{t} \log_e \frac{I_0}{I}.$$

It is essential that the radiation should be strictly monochromatic and only crystal-reflected radiation is adequate for the purpose. This is due to the rapid variation of the absorption coefficient with wave-length. In fig. 2 the two-crystal goniometer is shown set up for making these measurements. The goniometer has been turned at right angles to its position in fig. 1, and the additional parts used in this measurement are shown darker. The X-rays pass through the absorbing plate which is mounted on the small disk A. This disk is carried on a rod attached to

ne frame supporting the goniometer heads. When the frame moves ong the horizontal track, as it would do normally in order to inter- nange the positions of the two crystals, the disk A is moved sideways rough 3 mm. By covering the opening in the centre f the disk with two absorbing layers placed side by de, one of a standard substance, e.g. nickel, and the ther of the mineral under examination, it is possible arrange that the X-rays pass alternately through e two absorbers. The thicknesses of these absorbers re adjusted so that the absorption for them both is pproximately the same. After passing through the bsorber, the X-rays enter the collimator B, which ermits a beam $\frac{1}{2}$–1 mm. in diameter to pass through . This beam then falls on a stationary crystal plate C orientated that it reflects the characteristic copper adiation. By omitting the bar which normally con- ects the two goniometer heads together the left-hand rystal can remain stationary in any desired orienta- ion. The crystal C is long enough to reflect the X-ray eam equally well in both positions of the goniometer ead. Two areas of the crystal 3 mm. apart reflect the X-ray beams emerging through the two absorbers, ut it is easy to test the equality of the reflecting power f these adjacent points on the crystal surface simply by repeating the xperiment with the absorbers interchanged. After reflection from the rystal C, the X-ray beam strikes the photographic film which is mounted n the quarter-cylindrical camera D. This camera is mounted on the right- and goniometer head and moves sideways when the absorbers are nterchanged and rotates through a certain angle during the time that he X-rays are passing through the specimens. This process is achieved y the instrument in the following way. Suppose initially that the left- and absorber is in the X-ray beam and the motor is in operation. The camera is rotating and the monochromatic part of the radiation is being steadily reflected on to the film. In this way a straight vertical line is obtained on the left-hand side, fig. 7. After the screw-driven carriage has moved from the right to the left and back again the right-hand absorber comes into the X-ray beam and the reflected X-rays trace out he right-hand vertical line of fig. 7. The exposure may last several ours, during which time the absorbers are interchanged many times. After exposure for a sufficient time the film is developed and the

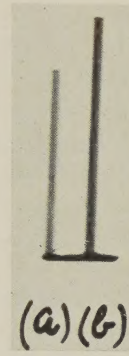

FIG. 7. Two traces produced by the crystal-reflected radiation after passing through absorbing plates of (*a*) biotite, (*b*) nickel.

blackening of the streaks is compared either visually or, better, by a micro-photometer. The simplest procedure is to repeat the experiment with different thicknesses of nickel until that thickness is found which has the same absorption as the specimen under test.

There are two important considerations which affect the conditions of the measurement. The first is concerned with the accuracy of measurement of the thickness and the second with the filtering action of the absorber, if the radiation is not entirely monochromatic. The first requirement is that the thickness shall be great enough to enable it to be determined with a specified accuracy, say 1 %. A micrometer screw gauge normally measures with an accuracy of 0·0002 in. or 0·0005 cm. To obtain an accuracy of 1% in the measurement of the thickness it is necessary to use a plate 0·05 cm. thick. Such a plate will reduce the intensity to 1/22,000 of its incident value if the absorption coefficient is taken as 200 cm.$^{-1}$ The length of exposure required, with such a reduction of intensity by the absorber, is some 6 hours. This is a long, but not unduly long, exposure. The second requirement for a satisfactory measurement is that the radiation shall be truly monochromatic. This is largely achieved by reflecting the radiation from a crystal but, with calcite at least, there is the possibility that radiation of wave-length 0·77 Å., i.e. half the wave-length of the characteristic $K\alpha$ radiation, will be reflected along with the $K\alpha$ radiation. Under normal operating conditions not only is $\lambda/2$ radiation part of the white radiation of the X-ray tube, but so also are $\lambda/3$, $\lambda/4$, and $\lambda/5$. To be quite certain that no sub-harmonic of the $K\alpha$ radiation is produced by the tube, the applied high tension must be kept below about 16 kV for copper anodes. If a crystal such as fluorspar or diamond is used as a monochromator the $\lambda/2$ radiation cannot be reflected for structural reasons and so the high tension can be raised to 24 kV, which is just not high enough to excite $\lambda/3$ radiation. The importance of the purity of the reflected beam arises from the difference in the absorption coefficients for λ and $\lambda/2$. For elements of atomic weight less than that of nickel the absorption coefficient for $\lambda/2$ radiation is about one-eighth of that for λ radiation. For elements of atomic weights above nickel and in the range within which Cu–$K\alpha$ radiation can be applied, there is little difference in absorption coefficient. When a large reduction in the intensity of the X-rays is introduced, by the necessity of using a specimen the thickness of which can be measured with sufficient precision the disturbance introduced by the $\lambda/2$ radiation is serious. To indicate how free from $\lambda/2$ radiation the beam must be we shall suppose that in

e beam emerging from the absorber the intensity of the $\lambda/2$ component 1 % of that of the λ. If the reduction factor for the λ radiation is ,000, then that for the $\lambda/2$ component is approximately 5 for elements atomic number less than that of nickel, and about 20,000 for nickel d elements of higher atomic number. Thus the $\lambda/2$ component is hanced about 4,000 times by passage through the absorber for ele- ents of low atomic number and not enhanced appreciably for nickel d elements of higher atomic number. Thus, in the range of atomic mbers within which the method described here is applicable, the tensity of the $\lambda/2$ component must be less than 1/400,000th part of e λ radiation in order to achieve a result accurate to 1 %. There is, course, no difficulty in doing this by keeping the high tension below e appropriate value.

To test the applicability of this method of finding the absorption efficient, cleavage flakes of biotite and phlogopite were balanced in rn against nickel. Biotite of thickness 0·012 inch and phlogopite of ickness 0·0165 inch had the same absorption, judged by visual inspec- on of the films, as 0·006 inch of nickel. The linear absorption, coeffi- ent of nickel for Cu–$K\alpha$ radiation is 438 cm.$^{-1}$, and hence the values for iotite and phlogopite are 220 cm.$^{-1}$ and 160 cm.$^{-1}$ respectively. On ferring to fig. 6 it will be seen that the values thus found experimen- lly correspond with those derived by calculation from the chemical mposition. However, the accuracy of the measurement of thickness this experiment was low and the chemical analysis of the specimen as not available, so that these tests can only be regarded as illustrating he method.

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Summary.

The main features of a two-crystal Weissenberg goniometer of the Wooster-Martin type are briefly described. The applications to two types of mineralogical problem are considered. (*a*) The determination of the intensities of reflection of a series of orders of a given plane or of the reflections from all planes having a common zone axis. Special attention is given to the measurement of absolute as well as relative intensities of reflection. (*b*) The determination of the X-ray absorption coefficients for certain iron-containing series of minerals with a view to a physical measurement of the percentage composition of iron in the mineral.

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